DESIGN OF NON-FLUOROUS CO_2 SOLUBLE COMPOUNDS

by

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University of Pittsburgh, 2009

Supercritical carbon dioxide ($scCO_2$) is an environmental friendly solvent for various chemical processes. In many cases $scCO_2$ is unable to replace organic solvents due to the low solubility of most polar and ionic materials in dense CO_2. Highly CO_2 soluble fluorinated polymers have been successfully designed but they are expensive and environmentally persistent. This project aims developing a non-fluorous compound which dissolves in CO_2 and thickens CO_2, thereby improving the performance CO_2 flooding enhanced oil recovery.

An attempt was made to generate CO_2-thickeners containing a CO_2-phile that promotes dissolution and a CO_2-phobe that induces viscosity-enhancing intermolecular associations. The initial research was directed at identifying the most CO_2-philic hydrocarbon-based polymer. Subsequently, associating groups would be incorporated.

Small sugar acetates are known to be extremely CO_2-soluble, but polymeric cellulose triacetate is CO_2-insoluble due to its crystallinity. Therefore a high molecular weight, low melting point polymer with per-acetylated monosaccharide side chains, poly (1-O-(vinyloxy)ethyl - 2,3,4,6 – tetra –O – acetyl – β – D - glucopyranoside), P(AcGIcVE) was synthesized. This polymer is second most CO_2-soluble hydrocarbon-based polymer and is slightly less CO_2-soluble than PVAc.

Amorphous poly(lactic acid) has also been shown to be highly CO_2 soluble over a broad range of molecular weight. The pressure required for dissolution greatly exceeds that associated with PVAc or P(AcGIcVE), therefore PLA is the third most soluble polymer in CO_2.

Oligo(vinyl acetate) is a particularly effective CO_2-phile. Poly(vinyl acetate), PVAc, remains the most CO_2-soluble high molecular weight, non-fluorous polymer that has yet been identified.

PVAc was selected as the base polymer for a copolymeric thickener. A pendant phenyl group was selected for viscosity-enhancing intermolecular associations because this mildly CO_2-phobic non-polar group was so effectively used for this purpose in a fluorinated CO_2 thickener previously designed by our group. Promising results were obtained with poly(vinyl acetate-co-vinyl benzoate$_{5\%}$). The viscosity of CO_2 increased by roughly 40% at a copolymer concentration of 1wt% and by 80% at 2wt%, at shear rates of 6200-5080 s^{-1} at 298 K. Therefore poly (vinyl acetate-co-vinyl benzoate$_{5\%}$) is the first documented non-fluorous CO_2 thickener capable of increasing the CO_2 viscosity substantially at dilute concentrations of ~1wt%. Unfortunately, the pressure required to dissolve this copolymer in CO_2 at 298 K (~65 MPa) greatly exceeds the MMP (Minimum Miscibility Pressure) of CO_2 floods at the same temperature (~10 MPa). Because we were not able to identify a hydrocarbon-based polymer more CO_2-philic than PVAc, it is doubtful that a non-fluorous, copolymeric thickener capable of dissolving in CO_2 at practical CO_2 flooding pressure conditions can be identified.

The only other non-fluorous polymer known to be more CO_2-soluble than PVAc is polydimethyl siloxane PDMS. Therefore, we evaluated three commercially available PDMS polymer with pendant phenyl groups. Two PDMS-based copolymers, poly(phenyl methyl siloxane)$_{10\%}$-co-(dimethylsiloxane) (Mw = 90,000 and 17000) were commercially available from

Gelest. Neither was soluble in CO_2 and copolymers with lesser degrees of phenyl methyl siloxane were not available.

An attempt was also made to design small molecules as thickeners. The first CO_2 soluble non-fluorous, acetylated hydrogen-binding compound and the first CO_2 soluble non-fluorous dendrimer were synthesized. It was postulated that these compounds would dissolve in CO_2 and then form linear macromolecules due to the hydrogen bonding between adjacent molecules. Critical features of these small, self-assembling molecules are the presence of strong and directional hydrogen bonding interactions between carbonyl oxygen and hydrogen in a bis-urea moiety, and the presence of multiple (two or four) highly acetylated "arms" on the periphery of the molecule that promote dissolution in CO_2. Although the first non-fluorous, CO_2-soluble hydrogen bonding compound (two arms) and hydrogen-bonding dendrimer (four arms) were designed, neither thickened CO_2. The hydrogen bonding compound with two arms did form brittle, microfibrillar, free-standing foams upon the removal of the CO_2.

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PREFACE

I wish to acknowledge an immeasurable debt of gratitude to a few individuals for their support and encouragement during my graduate studies. I owe my most sincere gratitude to my advisor, Dr. Robert M. Enick. No words can fully convey my respect and appreciation for him. His wisdom, knowledge and commitment inspired and motivated me through out these graduate years. He was always there to help and guide me, no matter how many times in a day I bothered him. It was only due to his valuable guidance, cheerful enthusiasm and ever-friendly nature that I was able to complete my research work and I am forever indebted to him for this. I would also like to thank Dr. Karl Johnson, Dr. Eric Beckman and Dr. Chapman for their guidance and support through out my PhD.

I wish to extend my warmest thanks to Dr Mark Thies and Jacob Crosthwaite for their support for collecting data, when I visited Clemson University. I would also like to thank Mark McHugh for his invaluable help on providing PLA high pressure data. Many thanks are also in order for Dr. Ik-Hyeon Paik and Dr. Hamilton at Yale University for their assistance in synthesis.

During this work I have collaborated with many colleagues for whom I have great regard, and I wish to extend my warmest thanks to all those who have helped me with my work. I would like to thank Dr. Lei Hong, Dr. Xin Fan, Dazun, Katie and Matt for their constructive discussions and support. I also want to express my appreciation to Rob Toplak, Bob Maniet, Ron Bartlett, Adrian Starke, Allison Crick, Rita Leccia and Pat Park for their assistance and cooperation.

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1.0 INTRODUCTION

Oil is an important source of energy. Currently, it supplies more than 40% of total energy demands and more than 99% of the fuel used in cars and trucks. All over the world, oil production is on decline. Since much of easy-to-find oil has been recovered, the present oil production is becoming increasingly costly. According to recently published data, oil output from all major oil companies is on decline trend. Exxon Mobil, for example, announced that its average oil output has fallen by 614,000 barrels per day in 2008. As for new projects, BP's Thunder Horse project in the Gulf of Mexico[1], for example, is finally coming online in 2008, with an anticipated output of nearly 250,000 barrels per day. But this one project has taken almost 20 years to complete, at a cost in excess of $6 billion. And Chevron's recent success with its Jack 2 project in the Gulf came at a cost of over $240 million for just one test well. The Jack 2 project is still years away from being a successful oil-producing prospect. With present technology, which depends on the natural pressure within the formation and subsequent injection of water in the formation to displace oil, nearly two barrels remain in the ground for every barrel produced. So it becomes extremely important to increase the production of oil by increasing the efficiency of enhanced oil recovery techniques (those used after the production from natural pressure and waterflooding approach uneconomic levels).

1.1 ENHANCED OIL RECOVERY

Oil recovery techniques have been grouped into three basic categories: primary, secondary and tertiary oil recovery. Primary recovery techniques exploit the pressure within the reservoir to drive oil from the porous medium to production wells with the assistance of production pumps (if necessary). When the reservoir natural pressure becomes too low to maintain economical production rate, then secondary recovery methods are applied. In secondary recovery an external force is applied to drive the oil to production well. This is typically done by injecting high pressure water or nitrogen into the reservoir. On average, the recovery of original oil after primary and secondary recovery operations is about 40 %, depending upon reservoir characteristics. Tertiary or enhanced oil recovery (EOR) is usually initiated near the end of economic secondary recovery to maintain oil production rates and thereby increase the amount of oil ultimately recovered from the reservoir. It typically involves injecting of $scCO_2$, steam, polymer solutions, sodium hydroxide solutions or surfactant solutions to improve oil flow from the reservoir.

Recent reports[2] from the US DOE suggest that in total there is 1,332 billion barrels of domestic oil resources which include original, developed and undeveloped fields, as shown in Figure 1.1. Out of this only 208 billion barrels is recovered by primary and secondary recovery. An additional 400 billion barrels can be technically recovered by using present enhanced oil recovery techniques. There are 724 billion barrels of unrecoverable oil in place; new technologies must be developed for the recovery of this portion.

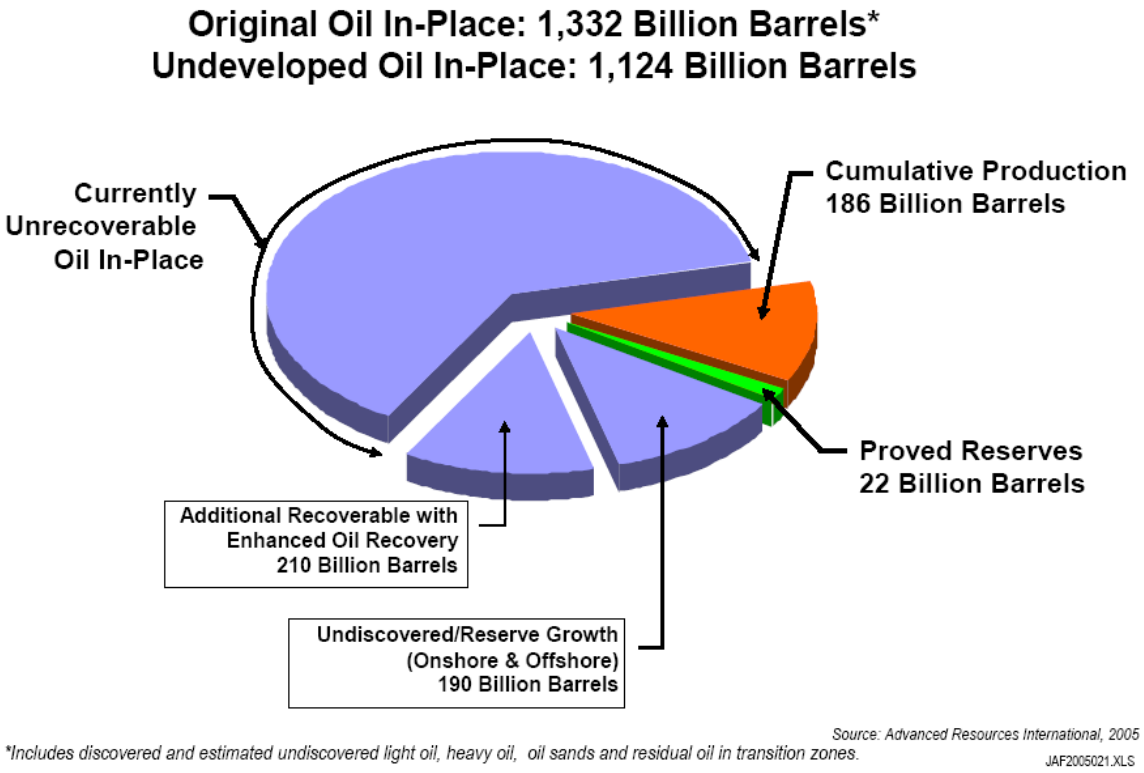


Figure 1.1: Original, Developed and Undeveloped Domestic Oil Resources.

All EOR methods fall into three major categories[3]: chemical, gas and thermal as shown in Figure 1.2. The purpose of injecting material or energy into the reservoir is to recover the trapped oil by reducing its viscosity or interfacial surface tension, increasing sweep efficiency, maintaining reservoir pressure, swelling the oil to increase its relative permeability or dissolving the oil into the solvent.

Thermal Method: The viscosity of oil decreases dramatically with increase in temperature. Therefore, hot water or high pressure steam is injected to increase the reservoir temperature. As a result, oil expands slightly and becomes significantly less viscous and moves towards the production well. This method is usually employed in the reservoir with heavy crude oil. In-situ combustion also aims at viscosity reduction and expansion. In this process air is injected and the viscous crude is ignited in the reservoir. This combustion reaction consumes a

small amount of oil and produces heat and which helps to dramatically lower the viscosity of the remaining oil.

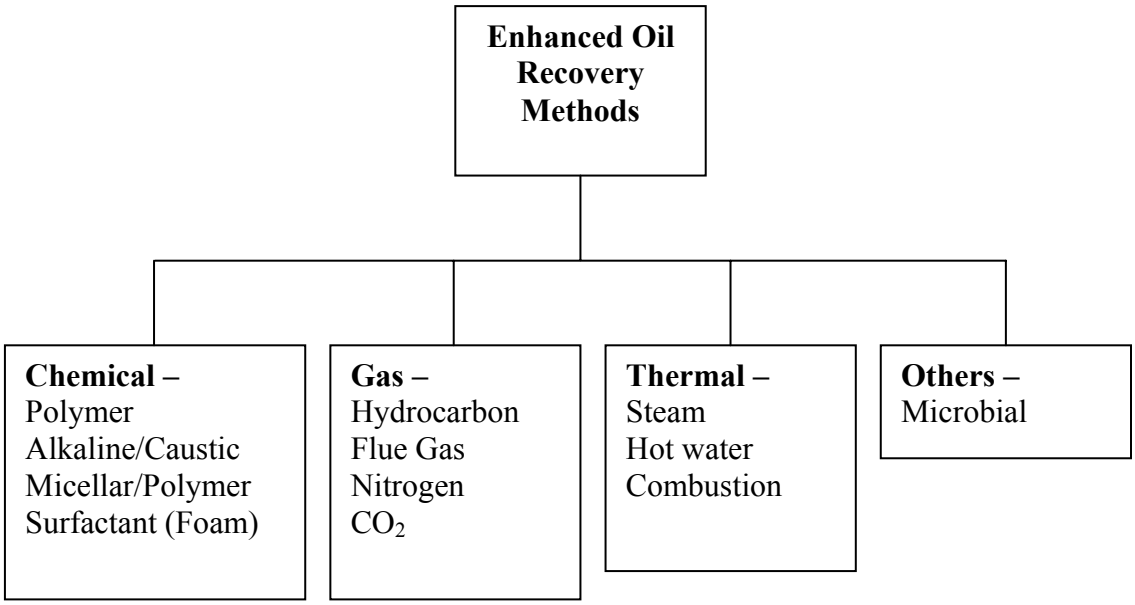


Figure 1.2: Enhanced oil recovery categories

Chemical Method: This method involves addition of alcohols, surfactants, polymers or bases in the reservoir. Micellar solutions are mixtures of surfactants (surface active agents), co-surfactants (alcohols for stability), electrolytes (salts for viscosity and interfacial tension control) and water. First the surfactant solution is injected in the reservoir followed by polymer-thickened water for mobility control. Caustic flooding is effective for the crude that has organic acid like naphthenic acids. It involves in-situ surfactant formation as a result of reaction between injected alkaline solution and acid present in the crude oil. This emulsification process helps to mobilize trapped oil. In polymer flooding, an aqueous solution of ultra-high molecular weight polymers is added to decrease the mobility of water in oil reservoir by increasing its viscosity.

Gas Injection: Depending on the properties of crude oil, rock and reservoir pressure different gases are injection to recover reaming oil. Gases like LPG or compressed liquid propane are miscible with oil upon first contact and are effective at low reservoir pressure.

Methane-rich gas, with some proportion of ethane, propane and butane , is not miscible with oil on first contact but can be effectively used for oil recovery. For example, for heavy crude oil, these gases get absorbed in the crude and develop a zone with is rich in C_1-C_4 and then form a miscible zone that moves towards production well. For crude oil rich in light components (C_2-C_6), at high pressure, methane-rich gases strip light components from the crude and develops a miscible front. (This process is typically employed until the gas production rates surge and the oil production rates drop significantly, at which point a pipeline and gas-processing facility are developed to recover the methane from the gas stream.) In CO_2 flooding, the dense CO_2 saturates the crude oil as a result oil swells, the oil viscosity decreases, the high pressure re-pressurizes the reservoir, and a miscible zone forms as the dense CO_2 extracts the lighter components from the crude oil. This multi-component fluid bank is indeed miscible with the crude oil ahead of it in the reservoir.

One of the most important and successful uses of CO_2 is in enhanced oil recovery (EOR) because it provides a way to recover substantial portion remaining oil present. An Oil and Gas journal survey shows that EOR contributed 649,000 bpd to US oil production in 2006[4]. Table 1.1 shows the US EOR production summary from 1986 to 2006. CO_2 flooding is the second most common EOR process used, next to steam flooding. However Table 1.1 shows that the oil production by steam flooding is now decreasing, while CO_2 flooding is flourishing. The total number of CO_2 injection projects for EOR has increased which has resulted in an increase in oil recovery by CO_2 injection (243,000b/d). CO_2 flooding is likely to continue expanding. Although current CO_2 projects obtain CO_2 at low cost from high pressure natural reservoirs of CO_2, future EOR projects may use anthropogenic CO_2 from power plants. Since CO_2 flooding technology is

mature and a valuable product (oil) is recovered, CO_2 EOR will be an economically, technically and politically viable means of sequestering CO_2 in the near future.

Table 1.1: EOR survey from oil and gas journal

	1986	1988	1990	1992	1994	1996	1998	2000	2002	2004	2006
Thermal											
Steam	468,692	455,484	444,137	454,009	415,801	419,349	439,010	417,675	365,717	340,253	286,668
Combustion insitu	10,272	6,525	6,090	4,702	2,520	4,485	4,760	2,781	2,384	1,901	1,3260
Hot water	705	2,896	3,985	1,980	250	250	2,200	306	3,360	3,360	1,776
Total	**479,669**	**464,905**	**454,212**	**460,691**	**418,571**	**424,084**	**445,970**	**417,675**	**371,461**	**345,514**	**301,704**
Chemical											
Micellar-polymer	1,403	1,409	617	254	64						
Polymer	15,313	20,992	11,219	1,940	1,828	139	139	1,598			
Caustic/alkaline	185										
Surfactant			20					60	60	60	
Total	**16,901**	**22,501**	**11,856**	**2,194**	**1,892**	**139**	**139**	**1,658**	**60**	**60**	**0**
Gas											
Hydrocarbon	33,767	25,935	55,386	113,072	99,693	96,263	102,053	124,500	95,300	97,300	95,800
CO2 miscible	28,440	64,192	95,591	144,973	161,486	170,715	179,024	189,493	187,410	205,775	234,420
CO2 immiscible	1,349	420	95	95				66	66	102	2,698
Nitrogen	18,510	19,050	22,260	22,580	23,050	28,017	28,117	14,700	14,700	14,700	14,700
Flue gas	26,150	21,400	17,300	11,000							
Other				6,300	4,400	4,350	4,350				
Total	**108,216**	**130,997**	**190,632**	**298,020**	**288,629**	**299,345**	**313,544**	**328,759**	**297,476**	**317,877**	**347,618**
Other											
Carbonated Water flood											
Microbial				2	2						
Total				2	2						
Grand Total	**604,786**	**618,403**	**656,700**	**760,907**	**709,094**	**723,568**	**759,653**	**748,092**	**668,997**	**663,451**	**649,322**

1.2 CO_2 IN ENHANCED OIL RECOVERY

CO_2 in EOR has been used by oil industry well over 50 years. CO_2 flooding has gained attention as one of the most technologically viable means of recovering undeveloped oil in place. CO_2 flooding efficiency strongly depends on reservoir temperature, pressure and crude oil composition. Figure 1.3 shows the effect of reservoir temperature and pressure on CO_2 flooding mechanisms. These mechanisms are broadly divided into 5 categories: -

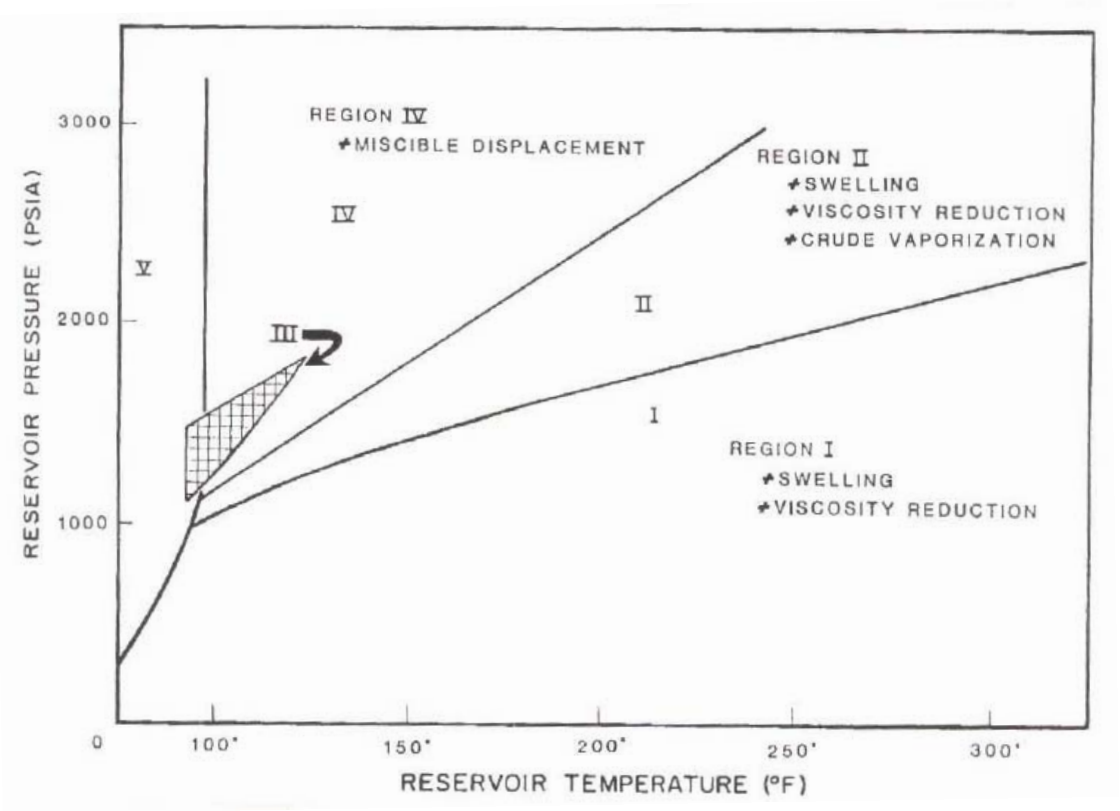


Figure 1.3: Temperature and Pressure effect on CO_2 flooding[3]

Low Pressure (Region I): At low pressure reservoir, CO_2 flooding depends on the solubility of oil in the crude oil. Once the injected CO_2 comes in contact with crude oil, the CO_2 dissolves in the oil swells the oil. Swollen oil droplets force water out from the pores and create favorable flow conditions for the oil by increasing its saturation in the pores and its relative permeability. As crude oil becomes saturated with CO_2, there is drastic decrease in the crude oil viscosity (about one-tenth to one-hundredth of original viscosity), which facilitates the displacement of the oil to the production wells. Once the CO_2 injection is stopped, CO_2 comes out from the solution and continues to drive oil towards production well.

Intermediate Pressure and High Temperature (Region II): Mixture of CO_2+oil swells up to certain pressure. At even higher pressure values, the light components of crude oil start vaporizing into the CO_2 rich phase. Therefore, in addition to swelling of oil and viscosity reduction, as in region I, vaporization of hydrocarbon into the gas phase takes place at high temperature. It has been demonstrated that the C_5 - C_{30} hydrocarbon components of crude[5] will vaporize into CO_2.

Intermediate Pressure and Low Temperature (Region III): This region is very similar to region II. At same pressure as region II but at lower temperatures, CO_2 + oil mixtures demonstrate the swelling and viscosity reduction behavior but instead of vaporization CO_2 extracts the lighter components of crude oil and forms a CO_2-rich liquid front. Then this CO_2-rich phase contacts crude and extracts even more of the light components, and eventually this fluid becomes miscible with the crude oil. This process is called multiple contact miscibility.

High Pressure (Region IV): In this region CO_2 swells oil, reduces its viscosity and vaporizes crude oil. But this vaporization, multiple contact miscibility, of crude oil is so fast that

it occurs in very short time and reservoir distance. Therefore it is considered that CO_2 is essentially "first contact" miscible with oil.

Based on the above mechanisms CO_2 can be effectively used for EOR. For practical proposes CO_2-EOR is divided into two processes: miscible displacement and immiscible displacement. Miscible CO_2 displacement takes place under favorable temperature, pressure and crude oil composition, at which CO_2 become miscible with crude oil in all proportions shown in Figure 1.4. As described above, CO_2 is not miscible with oil on first contact. However, displacement tests in long cores and sand packed slim tubes indicate that dynamic displacement is possible above minimum miscibility pressure (MMP)[6] (the pressure at which oil recovery is essentially complete i.e. compressing CO_2 above MMP does not result in increase in additional oil recovery). When CO_2 is injected and is brought in contact with crude oil, initially its composition is enriched with vaporized intermediate components of the oil. This local change in the composition near the injection well results in the development of a miscible zone between oil and CO_2, within a relatively short distance from the injection well. For the effective mixing of oil and CO_2, this process should take place above MMP. The value for MMP depends on reservoir temperature, pressure and crude properties. This CO_2-oil interaction makes oil swell and reduces its viscosity. As a result it improves the oil recovery rate and ultimate amount of oil recovery (relative to continued water flooding).

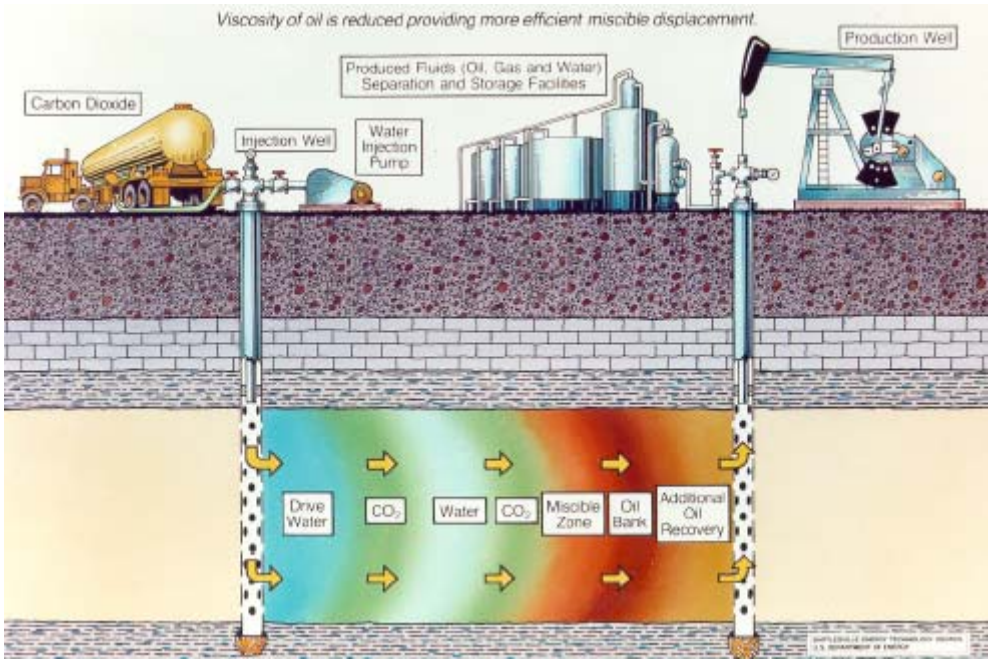


Figure 1.4: A schematic of water-CO_2 EOR operation

Immiscible CO_2 displacement takes place when the reservoir pressure is below the MMP or the crude oil is not miscible with CO_2, typically because the reservoir is so shallow that it cannot withstand the MMP requirement. Even when crude oil is not miscible with CO_2, increased oil recovery occurs due to oil viscosity reduction, oil swelling and reduction in surface tension.[7]

1.3 MOBILITY REDUCTION

Water-alternating-gas process (WAG): Current Industrial State of the Art: Dense CO_2 is much less viscous than the oil and water in the reservoir. As a result, the mobility (relative permeability/viscosity) of CO_2 is very high as compared to the oil and brine. Although a fluorinated thickener has been developed at the University of Pittsburgh, no commercial CO_2 thickener has ever been identified, therefore industry efforts have been directed at reducing the

relative permeability of CO_2 using other techniques. The simplest way to accomplish this is by introducing alternative slugs of brine and CO_2. This reduces the CO_2 saturation in the reservoir, which diminishes the relative permeability[3, 8] and the CO_2 mobility. This process is shown in Figure 1.4. WAG requires water injection equipment, delays the injection of the specified amount of CO_2, may inhibit the mixing of CO_2 and oil within the porous media, increases the amount of water production, and necessitates post-production water-oil separation processes and water re-injection equipment.

CO_2 Foam Flooding: Mobility reduction has also been proposed via generation of CO_2 foams in-situ. This concept involves the alternate injection of CO_2 and aqueous surfactant solutions. Foams can exhibit remarkable mobility reduction in porous media, especially at the lab scale[9, 10]. Further oil recovery could have increased due to oil emulsification, wettability changes and interfacial tension reduction. A pilot test, however, was discouraging primarily due to surfactant loss via adsorption. Further, the low viscosity, low density CO_2 may not flow into the same portions of the reservoir as the surfactant solution, especially in heterogeneous formations. Therefore CO_2 foam floods are not commercially used at this time.

1.4 CO_2 FRACTURING

CO_2 slurries of propping agent (such as sand) are used for the production of natural gas from reservoirs with low permeability[11-13]. Further, it may be undesirable to employ aqueous solutions as fracturing fluids in the candidate reservoir due to brine relative permeability increases and gas relative permeability reduction along the vertical fracture faces through which the gas is expected to flow. In this process, CO_2 is injected into the formation at extremely high

pressure (e.g. 10,000 psia) until the formation fractures as indicated by a sudden and dramatic decrease in pressure (e.g. 5000 psi). At this point, a slurry of CO_2 and sand is injected into the well in order to prop the 1/8" – 1/4" wide fracture open before it collapses upon itself, which typically takes about one minute. This creates a narrow, high permeability, sand-packed channel for the gas to flow from the formation to the well. This process is efficient when the fracture is deep, wide and propped open with large sand particles. The advantage of the CO_2 fracturing is that it eliminates the formation damage associated with conventional aqueous fluids or aqueous foams and reduces the cost of frac fluid cleanup and disposal. The main disadvantage of CO_2 fracturing is the low viscosity of CO_2. As a result CO_2 is not able to carry high concentrations of large proppant particles, which would yield a dramatically more permeable fracture.

1.5 PROBLEMS WITH CO_2 FLOODING

Theoretically, nearly all the oil remaining in the reservoir after a CO_2 flood could possibly be recovered if it is swept by the CO_2 at the MMP (this is achieved in small core lab tests), but in the field recovery is limited to about 20%. Reasons for this low recovery are:

- Unstable flow (fingering, shown in Figure 1.5) of CO_2 i.e. CO_2 is more mobile than oil or water being displaced. (Mobility is permeability/viscosity.) Early breakthrough of CO_2 results; i.e. CO_2 coming out of production well long before all the oil is removed due to high CO_2 mobility. (shown in Figure 1.6)
- Low density of CO_2 (at MMP) relative to oil causes gravity override, which inhibits the contact of CO_2 with oil in the lower portion of reservoirs.

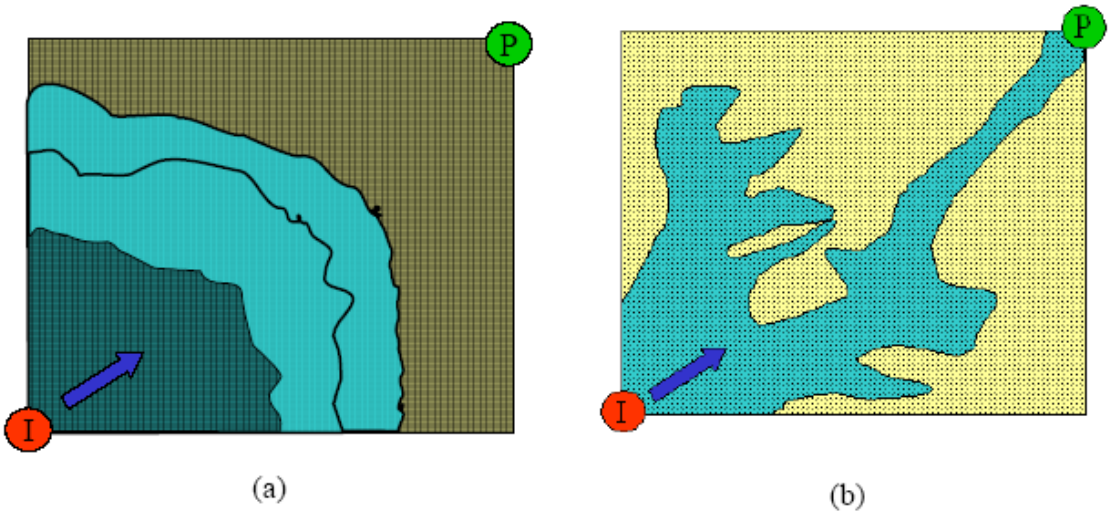


Figure 1.5: a) Ideal flow of CO_2 from injection well (I) to Production well (P) for maximum oil recovery b) Viscous fingering of CO_2 leaving behind large volume of oil trapped.

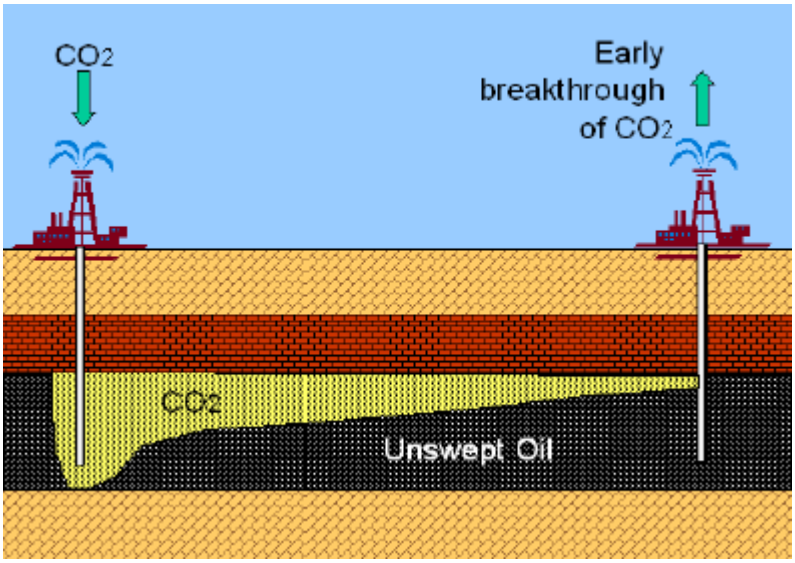


Figure 1.6: Early breakthrough of CO2 resulting in low areal and vertical sweep efficiencies.

It is not practical to increase the density of CO_2 by several tenths of a g/cc at a specified temperature and pressure via use of dilute concentration of additives, nor is it feasible to significantly decrease the permeability of CO_2 in the formation without introducing large

volumes of brine (WAG). It *is* conceivable, however, to make significant increase in viscosity via the introduction of dilute amounts of a thickener (oil and water thickeners that are effective at concentrations of 0.1-1 wt% are commonplace). **Therefore this work will focus on increasing the viscosity of CO_2 to a level comparable to the viscosity of the oil being displaced via the introduction of a dilute concentration of a hydrocarbon-based thickener.**

2.0 CO_2 AS A SOLVENT

Carbon dioxide is a small, linear, and symmetric molecule where carbon is covalently bonded to oxygen. In the past few decades there has been a great deal of development in the use of supercritical carbon dioxide ($scCO_2$), especially in petroleum engineering applications. The supercritical phase actually bridges the gap between liquid and gaseous states by offering gas-like diffusion rates and liquid-like solvent densities. Figure 2.1 represent the phase diagram for CO_2.

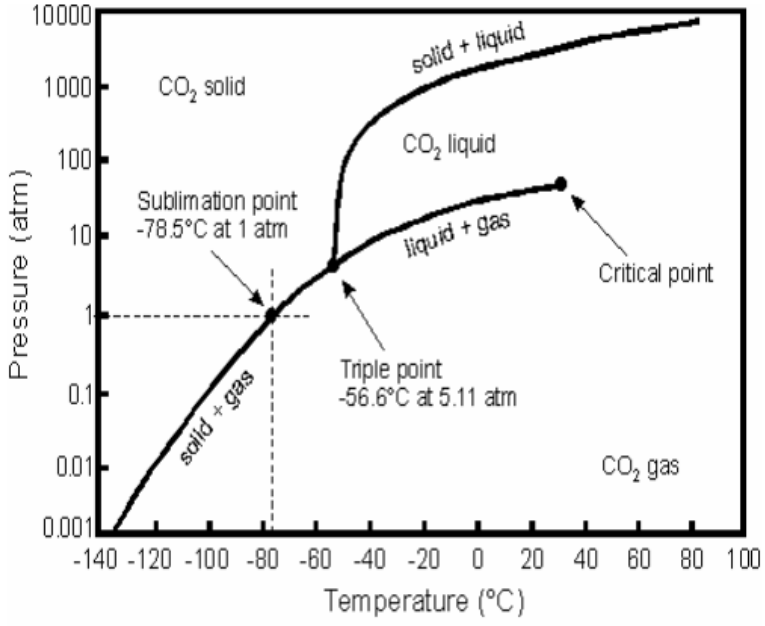


Figure 2.1: Temperature phase diagram for CO_2[14]

Supercritical carbon dioxide has gained a considerable attention as an environmentally acceptable alternative to organic solvents in many chemical and petroleum engineering

processes[15-17]. CO_2 is non-toxic, inexpensive for EOR (refrigerated CO_2 tankers delivered to frac jobs are not inexpensive), non-flammable, readily available and easy to remove (and recover) at the end of the process via de-pressurization (and re-compression). It is also a high pressure process (roughly 1000 or more psi), however, that often requires significant capital costs. Because of these properties, CO_2 is widely recognized as a green solvent. Some of the industrial examples where CO_2 has replaced organic solvents are the Dupont facility for producing fluoropolymers in $scCO_2$-based solvent, coffee decaffeination, and dry cleaning technology based on liquid CO_2[18]. CO_2 flooding is the largest industrial use of CO_2 as a solvent in the country; about 1.5 billion scf/d of natural CO_2 are used for EOR. Polymer, food[19] and pharmaceutical industries[20, 21] may use CO_2 for extraction/separation steps because of its pressure-adjustable solvent strength and non-toxic nature. There has been an on-going effort to develop new CO_2-philic polymers, oligomers, dispersants chelating agents, catalysts and surfactants which could enhance the potential of CO_2 as a processing fluid[19-24].

2.1 THERMODYNAMIC PROPERTIES OF CO_2

Despite these successes in niche markets, $scCO_2$ technology has not been as successful in many other technologies, primarily because CO_2 is a feeble solvent for polar and/or high molecular weight compounds. Physical properties of CO_2 and various supercritical solvents are in Appendix A. CO_2 was considered as an alternative solvent for hydrocarbon because of its low dielectric constant as compare to hydrocarbons. But it is not good solvent for long chain hydrocarbon systems[25]. Raveendran et al[26] has described CO_2 as a non-dipolar solvent system. Although carbon dioxide has no permanent dipole moment, the electronegative oxygen atoms

impart an especially large quadrupole moment to CO_2[27, 28]. It is this quadrupole moment[29] that gives CO_2 the potential to be an effective solvent for certain polar solutes. There is a charge separation in the CO_2 molecule with the bond electron density being polarized more toward the oxygen atoms, leaving the carbon atom with a partial positive charge and the two oxygen atoms with partial negative charges as shown in Figure 2.2.

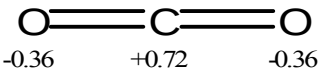


Figure 2.2: Charge distribution in CO_2

In order for a polymeric material or any other solute to dissolve in a given solvent, the Gibbs free energy of mixing, ΔGmix, must be negative and at a minimum. The Gibbs free energy of mixing is given by

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad \textbf{Equation 2.1}$$

where ΔH_{mix} and ΔS_{mix} are the change of enthalpy and entropy of mixing, respectively. The enthalpy of the system depends on the polymer segment-segment, solvent-solvent and polymer segment-solvent interaction energies. Thus the CO_2 soluble polymer is required to have weak polymer segment-segment interactions and strong polymer segment - CO_2 interactions. The balance of these interactions in a solution is described by the interchange energy[30], ω, defined as

$$\omega = z\left[\Gamma_{ij}(r,T) - \frac{1}{2}(\Gamma_{ii}(r,T) + \Gamma_{jj}(r,T))\right] \qquad \textbf{Equation 2.2}$$

where z is the coordination number and Γ is the potential energy, which is defined as

$$\Gamma_{ij} \approx -\left[C_1\frac{\alpha_i\alpha_j}{r^6} + C_2\frac{\mu_i^2\mu_j^2}{r^6kT} + C_3\frac{\mu_i^2Q_j^2}{r^8kT} + C_4\frac{\mu_j^2Q_i^2}{r^8kT} + C_5\frac{Q_i^2Q_j^2}{r^{10}kT} + \text{complexformation}\right] \qquad \textbf{Equation 2.3}$$

where α is the polarizability, μ is the dipole moment, Q is the quadrupole moment, $C_{1\text{-}5}$ are constants[31], r is distance between the molecules, k is Boltzmann's constant and T is absolute

temperature. Equation 2.3 only gives us the qualitative idea of polymer segment-CO_2 interaction because the polymer chain length is not taken into consideration. Dispersion interaction, the first term in equation 2.3, depends only on polarizability of the compound and the distance between CO_2 and polymer. This suggests that, as CO_2 has low polarizability, the polymer should have high polarizability in order to be soluble in CO_2 otherwise high pressure will be required to dissolve it in CO_2. The next three terms in equation 2.3 represent dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions. Although CO_2 has zero dipole moment, it has a substantial quadrupole moment over short distances. This quadrupole moment has a negative effect when a non-polar polymer is dissolved in CO_2 at low temperature because CO_2 quadrupole interactions will dominate the interchange energy (equation 2.3), therefore the polymer should be slightly polar (CO_2 is a reasonable solvent for slightly polar molecules). The critical point of the mixture, i.e. the lowest pressure at which molecule is soluble in CO_2, rises sharply with the increase in molecular size. Therefore high molecular weight polymers exhibit limited solubility.

Very limited amount of work has been done on CO_2 dimer and trimer systems to study CO_2 self interactions. Miller et al[32] and others have shown that a CO_2 dimer can interact in parallel and T-shape geometry as shown in Figure 2.3.

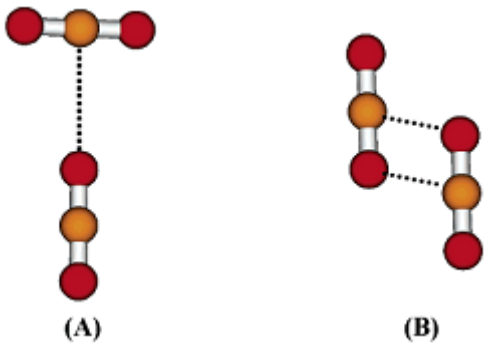


Figure 2.3: Optimized geometries (A) T-shape and (B) parallel of CO_2 dimer[26].

To study the CO_2 interactions in liquid state, modeling of CO_2 trimer was done by Nesbitt et al[33]. By doing IR spectral studies they demonstrated that CO_2 can foam cyclic and non-cyclic trimers; but the cyclic trimer was more abundant. Tsuzuki et al[34] have done *ab initio* calculation on these structures and concluded that non-cyclic structure is more thermodynamically stable.

Another complex interaction which is electron accepter-donor interaction also plays very important part in making polymers CO_2 soluble. It has been shown through the use of IR spectroscopy[35] that polymers possessing electron-donating functional groups display Lewis acid-base interaction with carbon dioxide with carbonyls, acetates and ethers. The interaction is between carbon of CO_2 which acts as Lewis acid and the oxygen present in the side chain of the polymer which acts as Lewis base[36].

Hydrogen bonding (C-H…O) is also reported[37] which act along with Lewis acid-base interaction in a systems having hydrogen atom attached to carbonyl carbon or α carbon. Figure 2.4 shows three different type in which CO2 can interact with carbonyl group.

Figure 2.4: CO_2 complex involving hydrogen bonding and CO_2 – Lewis acid-base interactions. Red represents oxygen, dark grey is carbon and small light grey is hydrogen.[38]

Kazarian et al[35] investigated the interaction of carbon dioxide with polymers and demonstrated that the polymers possessing the electron-donating group (e.g. carbonyl groups) exhibit specific interactions with CO_2 which are Lewis acid-base nature. Raveendran et al showed that in addition to Lewis acid-base interaction there is an additional stabilizing

interaction (hydrogen bonding) which helps in solvation of polycarbonyl moieties with hydrogen atoms attached directly to the carbonyl carbon. McHugh et al were the first to note that polyvinyl acetate exhibited remarkable solubility in CO_2. Our group along with Mark McHugh and Zhihua Shen of Virginia Commonwealth University, studied a wide range of polymers and found that only three oxygenated hydrocarbon polymers are capable of dissolving in CO_2 at 5 wt % or more[39] at pressures below 250 MPa. Those are, in order of decreasing CO_2 solubility, poly(vinyl acetate), high molecular weight amorphous poly(lactic acid) and poly(methyl acrylate).

Entropy of mixing is also plays an important in creating a single phase solutions. For high entropy polymer should have high free volume and high chain flexibility which results in low glass transition temperature of the polymer (Tg). Polymers with low Tg are more likely to dissolve in scCO_2 then with high Tg. Entropy becomes more important in polymers with high molecular weight because at high molecular weight chain flexibility decreases which results in less no of conformation. Branching of the polymer helps to increase the free volume. From a thermodynamic point of view, a balance between enthalpy and entropy is required for successful design of a CO_2-soluble polymer.

In light of all of these considerations, a polymer with , a slightly polar character, sites for Lewis acid : Lewis base interactions, sites for hydrogen bonding with CO_2, low glass transition temperature, branching and CO_2-philic functional group is an ideal candidate that will dissolve in CO_2.

3.0 RESEARCH OBJECTIVE

3.1 PREVIOUS ATTEMPTS TO THICKEN CO_2

The efficiency of CO_2 flooding and CO_2 fracturing can be increased if we can decrease the mobility of dense CO_2. Two ways of doing this are to either use a surfactant to form a foam (emulsion) or to use a thickener to directly enhance the viscosity of the single-phase CO_2 solution. Surfactant solutions have been used in the lab and a pilot test to generate a form when it is injected into the reservoir in alternating slugs with CO_2. (Current research in Dr. Enick's group is directed toward the use of CO_2-soluble surfactants for in-situ foam generation, which would eliminate the need for alternating slugs of surfactant solution). The two benefits of using surfactant are that it can decrease the mobility of CO_2 and it can also be used to block the permeable zone created in water flooding. Direct thickeners are designed to dissolve in the CO_2 and increase the viscosity of CO_2 by a factor of 2-50. Furthermore, the thickener should tend to partition in the CO_2 rich phase rather than the oil or brine in the reservoir. Many attempts have been made to thicken CO_2 during the last two decades. ***The objective of this work is to identify an oxygenated hydrocarbon-based direct CO_2 thickener; foams will not be considered.***

In the 1980's, John Heller was the first group to work on the use of direct thickeners for CO_2. He and his coworkers evaluated the solubility of several commercially available polymers in liquid and supercritical CO_2. They concluded that polymers can not increase the viscosity of

CO_2 but they made some generalizations about the CO_2 soluble polymers. They found that CO_2 soluble polymers should be amorphous and atactic and the polymers that are soluble in water or are isotactic are not highly soluble in CO_2[40]. Taking these things into consideration, they also synthesized amorphous, atactic polymers but they were only slightly soluble in CO_2. They also synthesized hydrocarbon-based telechelic ionomers as CO_2 thickener. These are low molecular weight polymers with ionic groups at each end of the chain. These polymers were successful thickeners for some non-polar solvents but had essentially no solubility in CO_2[41].

Heller et al. also tried to increase the viscosity by gelation of supercritical CO_2 with 12-hydroxystearic acid (HSA). The carboxylic acid head groups associate with one another when a pair of HAS molecules "face" one another, while the hydroxyl groups promote stacking of the HSA tails. HSA is insoluble in CO_2 but when used with co-solvent, 10-15% ethanol; it is completely soluble in CO_2 and formed translucent or opaque gels[42]. For controlling the mobility ratio, Heller group also tested various commercially available surfactants which form foams in dense CO_2; these foams did not have much influence on CO_2 mobility[43].

Terry et al[44] attempted to increase the viscosity of CO_2 via in-situ polymerization of CO_2-soluble monomers. They found that the resulting polymers were insoluble in CO_2.

Llave et al[45] used entrainers to improve CO_2 mobility. Entrainers are low molecular weight, CO_2-soluble compounds such as isooctane, 2-ethylhexanol and ethoxylated alcohol. Entrainers improved the viscosity of CO_2 but very high concentrations, for example, 44 mole% of 2-ethylhexanol resulted in 1565% increase in viscosity of CO_2.

Irani et al[46] considerably increased the viscosity of CO_2 by using silicone polymers. They were able to increase the viscosity of CO_2 by a factor of 90 by dissolving 6 wt% polydimethylsiloxane (MW = 197000) and 20 wt% toluene co-solvent.

In the last decade, DeSimone et al[47] reported that silicones and fluoropolymers exhibit higher degree of solubility in CO_2 as compare to other non-fluorous polymers. Soon this group identified first CO_2 thickener that did not require a co-solvent. They reported that 5-10 wt% of a fluoroacrylate homopolymer[48] can increase CO_2 viscosity by 3-8 fold.

Shi et al[49] synthesized CO_2-soluble fluorinated polyurethane telechelic disulfates which are soluble in CO_2 up to 4 wt % and can increase the viscosity by 2.7 fold. Semi-fluorinated trialkytin fluorides were soluble in CO2 below 18 MPa at 4wt% and increased the viscosity of CO2 by the factor of 3.3 times at 4 wt%.

To date only a single CO_2 thickener has been identified that is capable of order-of-magnitude type increases at dilute concentration that does not require a co-solvent; a random copolymer of **f**luoro**a**crylate and **st**yrene, dubbed polyFAST, developed by Enick, Beckman and coworkers[50]. The increase in viscosity was due to intermolecular π-π stacking of aromatic side chain functional groups. This was demonstrated indirectly in that analogous copolymers that had linear, rather than aromatic, side chains induced no viscosity increase. The optimum composition of the copolymer was found to be 29 mol% styrene and 71 mol% fluoroacrylate. Addition of 1.2 wt% of the copolymer increased the viscosity of CO_2 by the factor of 19 relative to neat CO_2 at the velocity of 0.00035m/s in a sandstone core[51]. This fluorinated thickener is too costly and environmentally persistent to be used commercially.

3.2 RESEARCH OBJECTIVE AND STRATEGY

The ultimate objective of this work is to make a thickener with CO_2-philic segments composed solely of carbon, oxygen and hydrogen that is soluble in CO_2 and can significantly increase the

viscosity of CO_2 at concentrations less than 1 wt%. This work does **not** investigate the use of surfactants as foaming agents for mobility reduction.

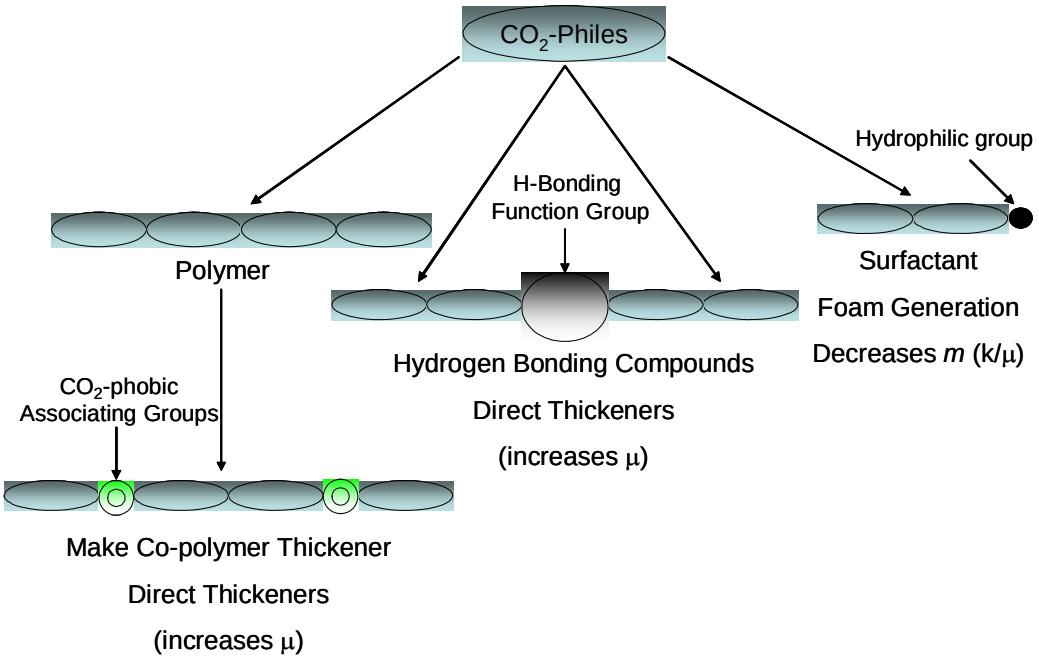


Figure 3.1: Strategy to make CO_2 soluble thickeners, hydrogen bonding compounds and surfactants.

The specific goal of this project is to **first** identify or design a highly CO_2-soluble oxygenated hydrocarbon oligomer. The **second** objective is to incorporate this oligomer as the CO_2-philic segment of thickeners, including copolymers and hydrogen bonding compounds that may increase the viscosity of CO_2 via intermolecular associations. The thickener, for example, should contain slightly CO_2-phobic associating groups, thereby allowing the thickener to dissolve in CO_2 and to associate and form viscosity-enhancing macromolecular networks. Two candidates will be considered; hydrogen bonding compounds and co-polymers.

The main emphasis of this DOE-sponsored research is the design of a co-polymeric thickener. The first step in the design of the co-polymer is to design or identify CO_2-philic

oligomers. The second step is to use that oligomer to make high molecular weight polymers. If the polymer is CO_2-soluble, it will then be modified to become a CO_2 co-polymeric thickener. Such modifications make the thickener less CO_2-philic because the associating groups are inherently CO_2-phobic, therefore the identification of CO_2 soluble polymer does not necessarily insure that a CO_2 thickener based on that polymer will dissolve in CO_2.

We have also assessed the ability of small hydrogen-bonding compounds to dissolve in CO_2 and then associate, thereby increasing the CO_2 viscosity. These compounds have one or two hydrogen bonding functional groups and at least two highly CO_2-philic "arms". This type of compound has been previously designed by Enick, Beckman, Hamilton and co-workers. Urea groups and fluoroalkyl "arms" were used to make a compound that dissolved in CO_2, made modest changes in viscosity, and then made low-density microfibrillar, brittle foam upon depressurization[52]. Our colleagues at Yale provided similar compounds for this project with non-fluorous, sugar acetate-rich arms. One of the H-bonding compounds, which will be detailed in a subsequent chapter, can be considered as a simple dendrimer.

In both cases (and even in the case of the CO_2-soluble surfactants that will be studied in the future), the identification of highly CO_2 soluble oligomers is required to design a CO_2-soluble thickener.

3.3 GENERAL GUIDELINES FOR MAKING CO_2 SOLUBLE POLYMERS

a) **Acetylation** usually increases the CO_2 solubility. For example poly(vinyl acetate) is the most CO_2-soluble, high molecular weight, oxygenated hydrocarbon polymer. Per-

acetylated monosaccharides[53], disaccharides, cyclodextrins and oligomers with up to four acetylated sugar repeat units are highly soluble in CO_2.

b) **Acetylation alone does not ensure CO_2 solubility**. Crystalline per-acetylated polysaccharides (e.g. cellulose triacetate) are CO_2 insoluble. PVAc, which has a pendant acetate associated with every other C in the polymer backbone, is very CO_2-soluble, yet poly(methoxy acetate), which has a pendant acetate associated with every C in the polymer backbone, is not soluble in CO_2 probably due to its extremely high melting point.

c) The polymer should be **amorphous** i.e. it should have flexible chains and high free volume. These properties are necessary to have high entropy of mixing and thus high solubility in CO_2. Branching increases the free volume of solute there by decreasing the intermolecular interaction between polymer segments. Eastoe et al[54, 55] has shown that AOT surfactant is not soluble in CO_2 but modified AOT, with higher branching at the tails end are CO_2 soluble.

d) **Carbonyl and ether groups** can also be used to design CO_2 soluble polymers. Molecular modeling has shown that interaction energy of ether-CO_2 is comparable with interaction energy of carbonyl-CO_2[56].

e) **Amine functional groups and hydroxyl groups should be avoided** in designing CO_2 soluble polymer. Self interactions between amine groups dominate all the interactions between CO_2 and polymer[57]. Similarly, hydroxyl groups are well known to be CO_2-phobic.

f) **Methylene spacer**s between polymer backbone and acetate group or any other pendent group should be avoided. For example, poly(allyl acetate), which has a methylene spacer

backbone and acetate group, was completely insoluble in CO_2. This is probably the most poorly understood, yet indisputable, effect in the design of CO_2-soluble polymers.

g) From thermodynamics' point of view, a polymer with slightly polar character, sites for Lewis acid : Lewis base interactions, sites for hydrogen bonding with CO_2, low glass transition temperature, branching and CO_2-philic functional group is an ideal candidate that will dissolve in CO_2.

4.0 POLYMERS

In an attempt to develop less expensive and environmentally persistent CO_2-soluble compounds, several investigators have investigated highly CO_2-philic derivative, composed solely of carbon, hydrogen and oxygen. For example, poly(ether-carbonate), (240 repeat units, 15.4 mole % carbonate) was soluble in CO_2 at 1 wt % at low pressure (14 MPa) and was comparable to poly (hexafluoropropylene) oxide with 175 repeat units (soluble for 1 wt % at 18 MPa). The solubility of poly(ether-carbonate) in $scCO_2$ is partly due to the high concentration of negative charge density on the oxygen atoms of each carbonate functional group[58]. The solubility of these polymers in CO_2 is strongly dependent upon the ratio of carbonates to ethers, it is somewhat difficult to synthesize polymers with a precisely desired ratio, and the cloud point pressures required to dissolve these polymers at concentrations as great as 5wt% have not been reported. (Cloud point pressures at 5wt% are commonly used to gage the CO_2-solubility of polymers.) Therefore, poly(ether-carbonates) were not further studied in this work. The acetate group was also recognized as having the potential to be very CO_2-philic and has the advantage of easy introduction into polymers or small compounds. As expected, an increase in the CO_2-solubility of siloxanes was observed with the addition of acetate side chains to silicone oil[56]. McHugh et. al. observed the significantly lower cloud point pressure of poly(vinyl acetate) relative to its isomer poly(methyl acrylate)[59], even though the molecular weight of the PVAc was significantly less than the PMA. Our subsequent joint study with McHugh substantiated that PVAc was more

CO_2-soluble than any other polymer composed solely of C, H and O[39] over a very broad molecular weight range. The later design of CO_2-soluble acetylated ionic surfactants[60, 61], and high CO_2-solubility of peracetylated sugars such as sorbitol [62], high molecular weight peracetylated cyclodextrins[63], and maltose octaacetate[64] successfully demonstrated the CO_2-philic nature of acetate group. The enhancement of CO_2 solubility via acetylation has also been studied by Wallen[53], who first reported the high solubility of glucose pentaacetate and galactose pentaacetate. Manke and co-workers recently provided a very detailed phase diagram for galactose pentaacetate in CO_2 by dew-point and bubble-point measurements and confirmed a substantial solubility of galactose pentaacetate in CO_2[65]. A two-point association involving, (1) a Lewis acid:Lewis base interaction between the oxygen in the acetate carbonyl group and the carbon of the CO_2; (2) a weak hydrogen bonding between the acetate methyl groups and the oxygen of the CO_2 is believed to be responsible for the thermodynamic affinity of the acetate group for carbon dioxide[37].

Based on the favorable CO_2-polymers interactions CO_2-philes were identified. The polymers were synthesized and phase behavior studies were done to check the solubility of polymer in CO_2.

4.1 PHASE BEHAVIOR EXPERIMENT

Polymers were evaluated in CO_2 at 298K and 70 MPa from 5wt % to 1wt %. Some of these polymers might be soluble in CO_2 at less than 1 wt % but those polymers that were not soluble to 1 wt % were highly unlikely to remain CO_2 soluble when modified by the inclusion of CO_2-phobic associating groups. Therefore any polymer that was not at least one weight percent

soluble in CO_2 is regarded as insoluble in this research. For the polymers which were soluble in CO_2, cloud point pressures were determined using a standard non-sampling technique involving slow, isothermal compression and expansion of binary mixtures of known overall composition. The cloud point pressure is designated as the highest pressure at which a minute amount of the denser, polymer-, H-bonding compounds- or dendrimer-rich phase remains in equilibrium with the CO_2-rich fluid phase. Typically, when this pressure is realized, the transparent single-phase solution becomes essentially opaque as the "cloud" of the second phase appears.

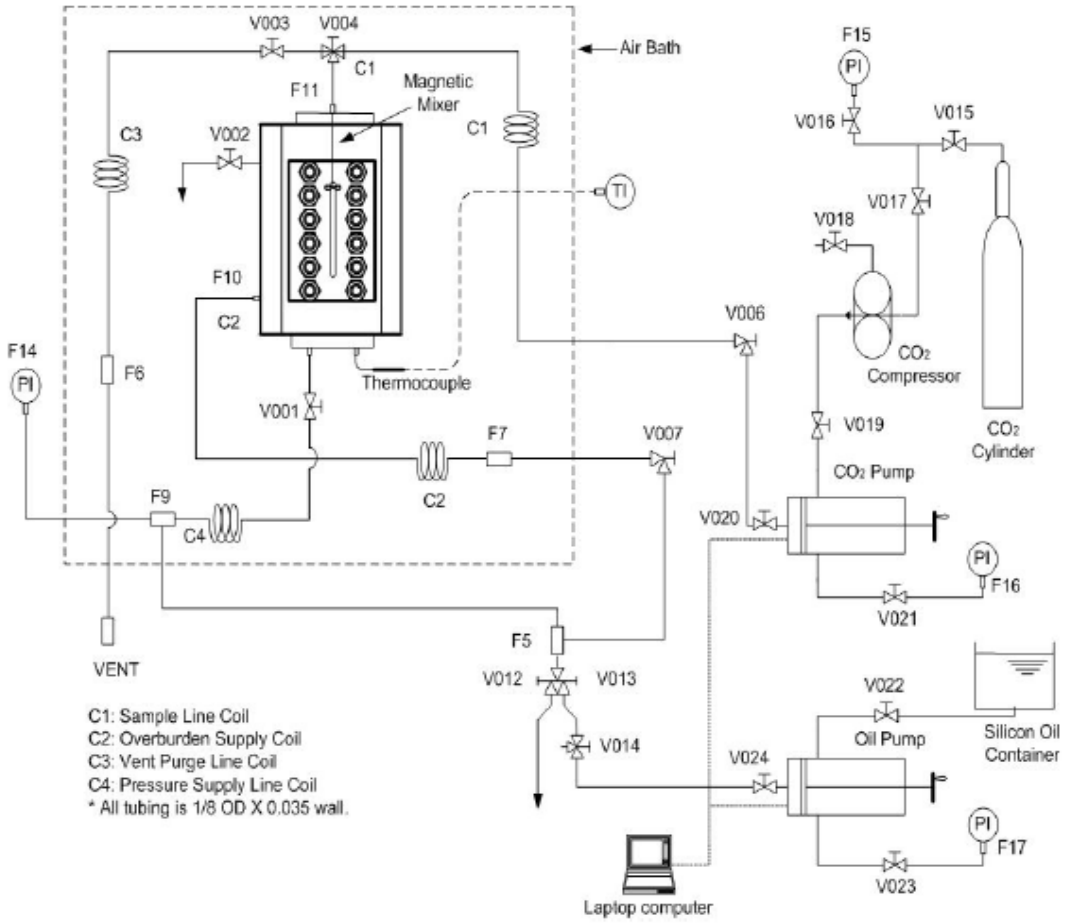


Figure 4.1: Schematic of phase behavior apparatus (Robinson cell)

Phase behavior studies were performed using high pressure, variable-volume, windowed cell, Figure 4.1, (formerly DB Robinson and Associates, now Schlumberger) retained in a

constant temperature air bath. Temperature range for the cell is -20^{o}C to 180^{o}C and can be pressurized up to 10000 psi. The maximum volume of the cell is about 110 cc. To do the phase behavior experiment, a known amount of polymer sample is place on the piston inside the glass quartz as shown in Figure 4.2. The piston can be moved up or down, thereby decreasing or increasing the volume of the sample chamber, by adding or withdrawing the overburden fluid (silicone oil) using a positive displacements pump. CO_2 is added to the cell and constant pressure is maintained by withdrawing overburden fluid. When the required amount of CO_2 is added, the cell is pressurized and mixed using magnetically driven stirrer until the single phase is obtained at very high pressure (up to 70 MPa). Then cell is then slowly depressurized by withdrawing overburden fluid until two phases were observed; the second phase may be droplets of liquid polymer or fine particles of a solid polymer. At the when no light can transmit through the sample, the pressure is considered to be the cloud point pressure, also known as the dew point pressure for liquid polymer droplets. The particles or droplets of the second phase would accumulate at the bottom of the cell for cloud or dew point measurements. The system is pressurized again and mixed to obtain single phase and depressurized until the two-phase pressure is again observed. For each weight percent, this process is repeated 3-4 times to obtain a consistent reading. Bubble point pressures were easily detected as the pressure at which the first bubble of a CO_2-rich vapor appeared. Liquid-liquid "bubble" points appeared as cloud points, but were distinguished by the droplets of the second liquid phase floating *up* to the top of the sample volume. Three phase pressures were easily detected as the pressure at which the first bubble of a CO_2-rich vapor would appear from a liquid-liquid system.

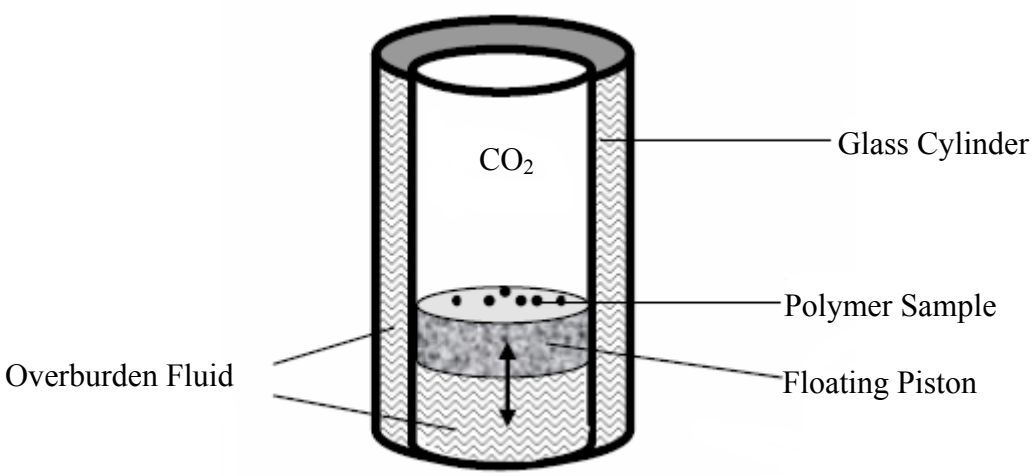


Figure 4.2: Schematic of glass cylinder with piston, polymer and CO_2

Based on the guidelines provided in the previous section new oxygenated polymers were tried.

4.2 POLY (VINYL PROPIONATE)

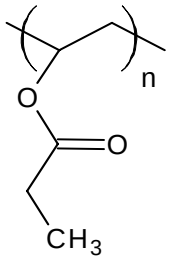


Figure 4.3: Poly (vinyl propionate)

Poly (vinyl propionate) (PVPp) is very similar to poly (vinyl acetate) (PVAc) but has a side chain terminated with ethyl group instead of methyl group. It was thought that increase in the length of side chain will increase the free volume of the polymer which will lower the glass transition temperature and thus might be more soluble in CO_2 than PVAc. Poly (vinyl

propionate) (30000 molecular weight and melting point 35°C) was purchased from Aldrich and was tested for its solubility in CO_2. It has lower glass transition temperature (Tg), 10^oC, as compare to poly (vinyl acetate) which has Tg of about 30^oC for the same molecular weight. It was found that poly (vinyl propionate) was not soluble in CO_2 although it did become a free-flowing liquid in CO_2. An increase in the side chain length in PVPp apparently acted as a hindrance to the Lewis acid-base interaction between polymer and CO_2, which are responsible for making PVAc CO_2 soluble. As result PVPp was not soluble in CO_2. (This polymer will be evaluated in a 20000 psia cell at Clemson during 2009.)

4.3 POLY (PROPYLENE FUMARIC ACID)

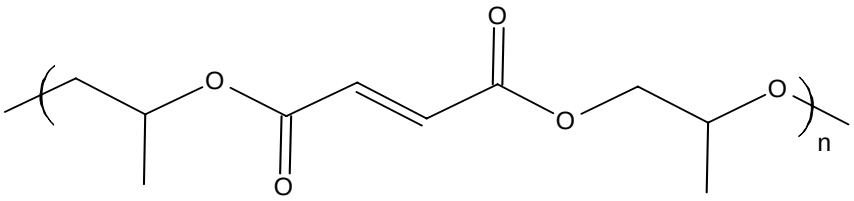


Figure 4.4: Poly (propylene fumaric acid)

Poly (propylene fumaric acid) (5000 molecular weight) has highly oxygenated backbone. This polymer was tried to determine the effects of oxygen in the backbone rather than on the pendent group. It melted in CO_2 but it was not soluble.

4.4 POLY (ACETOXYMETHYLSILOXANE)

The objective is to design a highly CO_2-philic polymer solely composed of C, O and H. Given the challenge of this task and remarkable solubility of siloxane polymers in CO_2, we decided to determine if acetylation of PDMS would further enhance the solubility of this polymer. This was the only Si-containing polymer that was studied.

4.4.1 Synthesis of poly(acetoxymethylsiloxane)

Material: Polymethylhydrosiloxane of average molecular weight 1600 was bought from Gelest and palladium acetate, acetic acid, and benzene was purchased from Aldrich and used without any purification

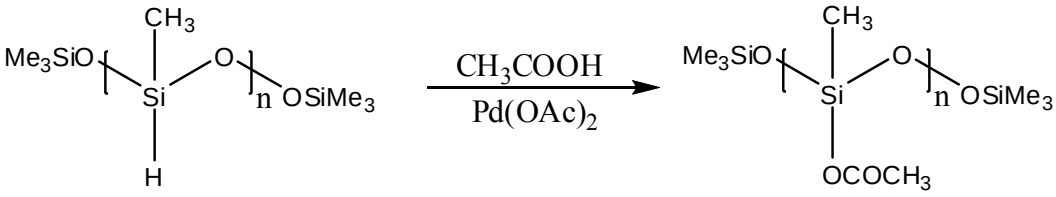


Figure 4.5: Reaction of poly (methylhydrosiloxane) with acetic acid to give poly (acetoxymethylsiloxane)

Synthesis: A mixture of palladium acetate (0.5mmol) and acetic acid (50mmol) in12 ml benzene was degassed by freeze-pump-thaw cycle. Poly (methylhydrosiloxane) (50mmol) was added to the mixture at 70°C. Evolution of gas (presumably H_2) was observed and the reaction mixture turned from yellow to black. The progress of the reaction was observed by IR by disappearance of the Si-H band at 2166 cm^{-1}.After the completion of the reaction, the catalyst precipitated and from the remaining colorless solution benzene was removed under vacuum to obtain poly(acetoxymethylsiloxane).

The resultant poly(acetoxymethylsiloxane) was very unstable and very quickly hydrolyzed to produce acetic acid while forming a cross-linked network which was not soluble in CO_2.

4.5 POLY(LACTIC ACID) (PLA)

Amorphous PLA, composed of a racemic mixture of the D- and L- isomers, was selected rather than crystalline sample because high melting point polymers are notorious for being difficult to dissolve in CO_2. A previous study by Mark McHugh [66] has demonstrated that high molecular weight (Mw = 84500 and 128450) PLA is soluble in CO_2 at pressures far in excess of those required for the dissolution of PVAc. However, in our study, the CO_2 solubility of PLA was studied over a wider range of molecular weight to determine if lower molecular weight PLA exhibited cloud point pressures more comparable to that of PVAc of comparable molecular weights. The effect of the end group composition on the CO_2 solubility of several very low molecular weight oligomers, Figure 4.6, was also determined.

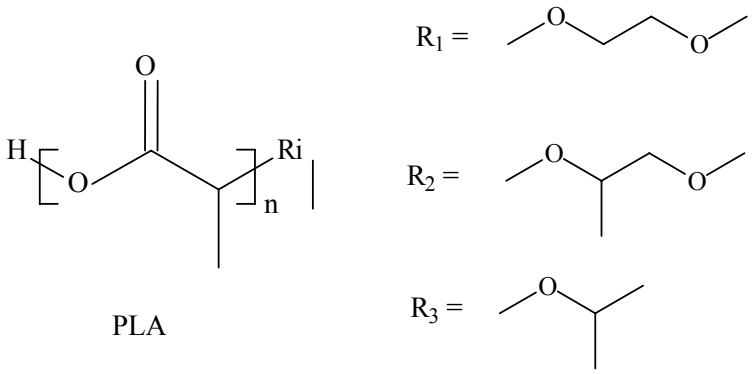


Figure 4.6: PLA oligomers with different end groups

Material: Amorphous PLA with acid end groups and inherent viscosity 0.17 dL/g, 0.45 dL/g and, 0.66 dL/g, which correspond to weight molecular weight of 12000, 55400 and 94500, respectively, were purchased from Lakeshore Biomaterials. PLA with different end groups (R_1 Mw = 5700 and 8300; R_2 Mw = 1265 and R_3 Mw = 900), Figure 4.6, were purchased from Polymer Source.

4.5.1 PLA phase behavior results

Different molecular weight samples of amorphous, acid-terminated PLA were dissolved in CO_2 at room temperature at a concentration of 5wt%. The resultant phase behavior is shown in Figure 4.7. As with PVAc, the cloud point curve corresponding to PLA is relatively flat over a broad range of molecular weight. However the pressure required to dissolve PLA ranges between 120 – 140 MPa at 298K; more than twice that required to dissolve PVAc in dense CO_2.

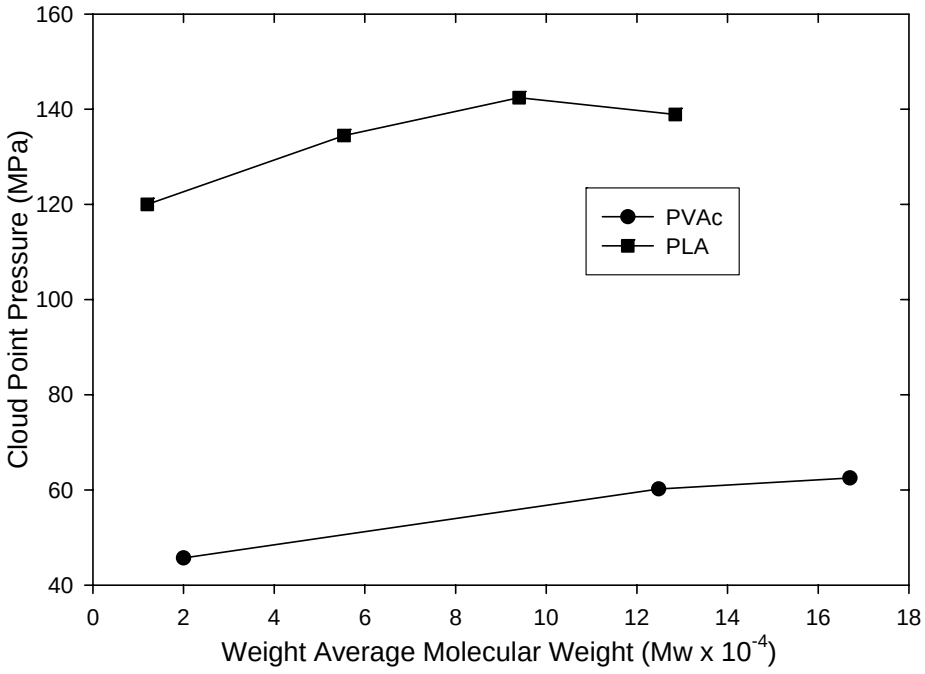


Figure 4.7: Cloud-point pressures at 5 wt% polymer concentration and 298 K for binary mixtures of CO_2 with poly vinyl acetate (■) and polylactic acid (●) as a function of weight average molecular weight. Data for Mw = 84500 and 128450 previously published by McHugh. PVAc data previously published[66].

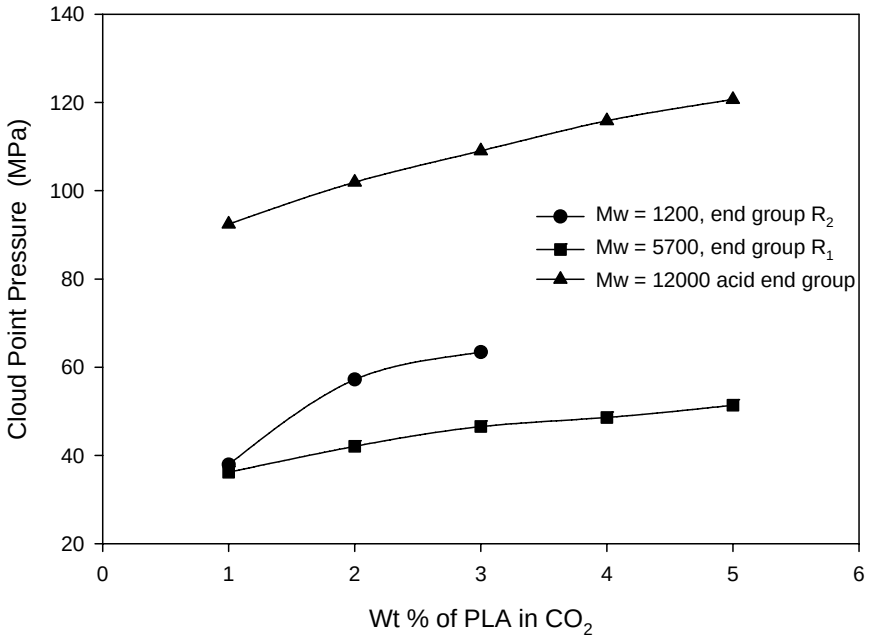


Figure 4.8: Phase behavior of low molecular weight PLA with different end groups in CO_2, cloud point data at 1- 5wt% PLA and 298K.

The CO_2 solubility of several very low molecular weight PLA oligomers was also determined over the 1-5 wt% range, Figure 4.8. (Because these samples were not acid terminated and the effect of the end group is recognized to be most significant at low molecular weights, the 5wt% cloud point data were not provided in Figure 4.7, which contains the higher molecular weight, acid terminated PLA data.) The R_1 end group, which is linear with two ether oxygens, seems to impart the greatest degree of CO_2 solubility. This is evidenced by a decrease in cloud point pressure, despite a molecular weight increase from 1200 to 4700, when the R_2 end group, which had two ether oxygen and a pendent methyl group, was replaced with the R_1 end group. When the end group contains only single ether oxygen, R_3, the PLA with Mw = 900 was insoluble in CO_2.

It is observed that solubility of low molecular weight PLA is quite comparable to low molecular weight PVAc. However with increase in molecular weight, the pressure required to dissolve PLA in CO_2 is almost double of PVAc for same molecular weight and weight percent.

4.5.2 Molecular Modeling

In an attempt to determine a more accurate understanding of why PVAc was remarkably more CO_2 soluble in CO_2 than amorphous PLA, *ab initio* calculations were employed.

Computational Methods: We constructed a model for poly(lactide) consisting of two repeat units, hereafter referred to as the PLA dimer (shown in Figure 4.9). The PLA dimer model was used to compute the interaction energies and binding configurations with CO_2. In order to compare PLA with PVAc on an equal footing in our calculations, we used an IPA dimer as a

reference for PVAc, which we have studied previously[67]. The IPA dimer, which will also be referred to as the PVAc dimer, is shown in Figure 4.10.

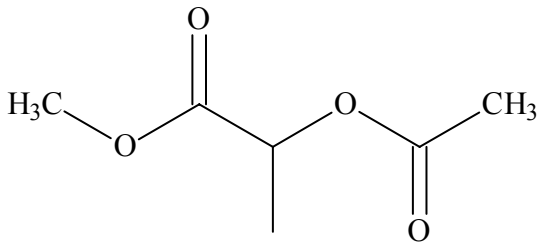


Figure 4.9: The structure of a compound with two repeat units of poly(lactide), (PLA dimer)

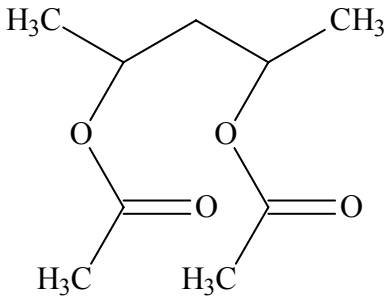


Figure 4.10: The structure of a compound with two repeat units of poly(vinyl acetate), PVAc dimer

We have used *ab initio* quantum chemical methods to calculate the interactions between CO_2 and the molecules of interest. The calculations include three steps. First, we made initial guesses for the binding configurations by randomly placing a CO_2 molecule around the important functional groups (ester and carbonyl oxygen) of the model molecules. Second, we used second order Møller-Plesset (MP2) perturbation theory along with the 6-31+G(d) basis set to optimize the configurations of the CO_2+model molecule systems. Finally, we used a larger basis set, aug-cc-pVDZ, to compute the binding energy for the optimized systems to improve the accuracy of the results. We have used counterpoise (CP) corrections to account for basis set superposition error (BSSE)[68]. We have used the average values of raw and CP corrected energies to approximate the complete basis set limit binding energies. This method has been shown to give reasonable estimates for the complete basis set limit binding energies [56, 69].

4.5.3 Theoretical Results

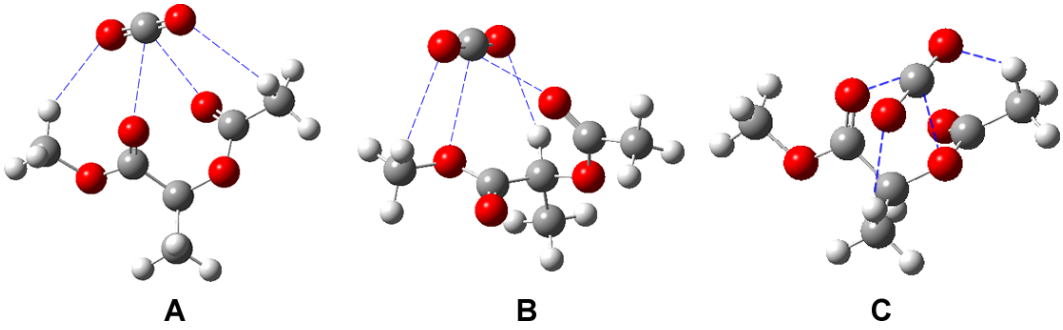


Figure 4.11: Three distinct binding configurations of CO_2/PLA dimer systems

PLA dimer: -We have identified three distinct binding configurations for CO_2/PLA dimer system, starting from six initial structures. The final binding configurations are shown in Figure 4.11. The calculated energies are listed in Table 4.1 along with the previously published results for three (different) configurations of the CO_2/isopropyl acetate (IPA) monomer (also referred to as the VAc monomer) system from Kilic et al[67] We can see from Table 1 that the interactions energies between CO_2 and the PLA dimer are much stronger than those between CO_2 and the IPA (VAc monomer) molecule. This is expected because the PLA dimer contains two acetate-like structures while IPA in this prior reference only has one. We note that the carbon atom in CO_2 molecule always binds with two oxygen atoms in the PLA dimer molecule and only binds with one oxygen atom in IPA molecule. The additional C-O interaction pair is responsible for the stronger interactions.

Table 4.1: The interaction energies for the CO_2/PLA dimer and CO_2/IPA systems. See Figure 8 for the definition of the configurations for the CO_2/PLA dimer system and for the corresponding definitions for the CO_2/IPA system.[67]

Configuration	Interaction energy (kJ/mol)	
	CO_2/PLA dimmer	CO_2/IPA monomer
A	-23.2	-14.8
B	-22.0	-14.2
C	-21.8	-15.9
Average	-22.3	-15.0

In order to make a more fair comparison between PLA and PVAc, we subsequently carried out calculations for CO_2 interacting with the IPA dimer (PVAc dimer) shown in Figure 4.10.

PVAc dimer: The PVAc dimer has a greater degree of conformational flexibility than the PLA dimer, and therefore the two pendant groups give rise to a larger number of rotational isomers. We have identified five distinct conformations corresponding to minima for the PVAc dimer; these are shown in Figure 4.12. The conformations are numbered from 1 to 5 based on the calculated energies, from the lowest to the highest. We set the energy of conformation 1 to be zero. The relative energies are then 5.4, 6.7, 9.6 and 15.5 kJ/mol for conformations 2 through 5, respectively. We have optimized multiple configurations of the CO_2/PVAc dimer system, starting from the five conformations listed in Figure 4.12. We have obtained seven distinct optimized geometries for the CO_2/PVAc dimer system, shown in Figure 4.13. The calculated energies for these binding modes are listed in Table 4.2.

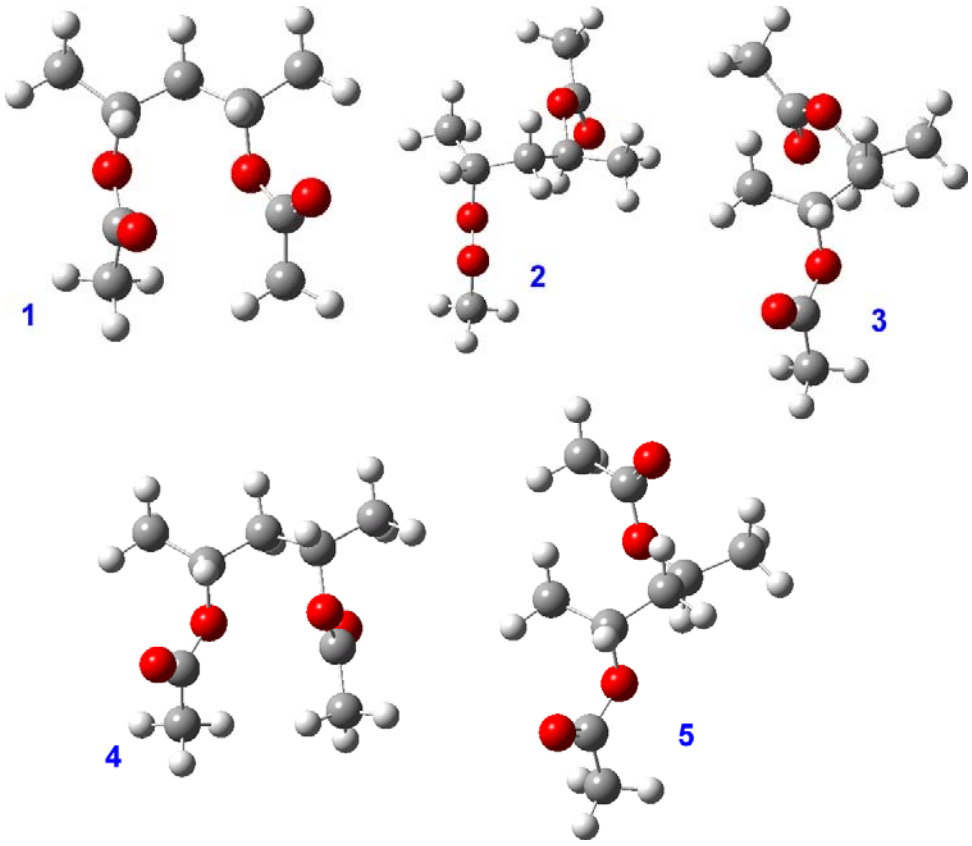


Figure 4.12: Five distinct conformational minima of the PVAc dimer molecule. They are numbered according to the calculated energies, from the lowest to the highest.

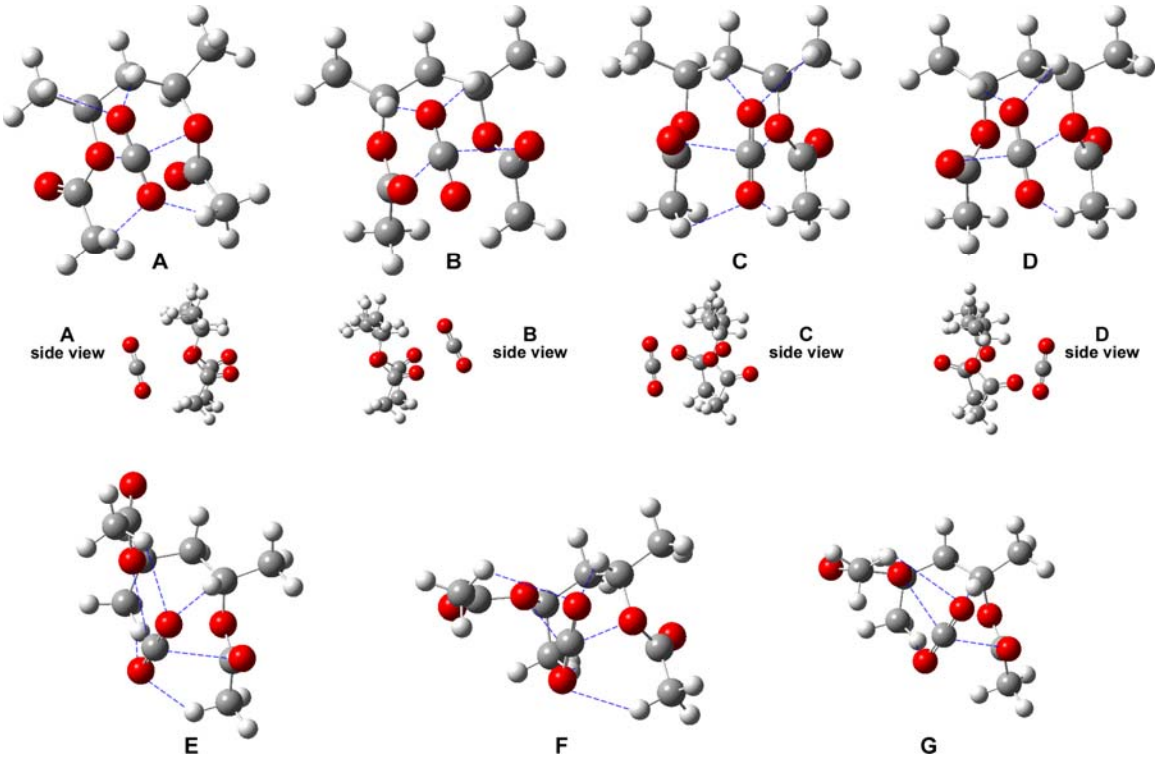


Figure 4.13: The optimized binding configurations for the CO_2/PVAc dimer system. The blue dashed lines indicate the primary interaction points between the two molecules.

Table 4.2: Interaction energies of CO_2/PVAc dimer system.

Configuration	Interaction energy (kJ/mol)
A	-22.0
B	-25.0
C	-25.4
D	-26.1
E	-24.7
F	-24.4
G	-22.3
Average	-24.3

The PVAc dimer molecule in binding modes A and B adopts essentially the same geometry; the difference in binding energy is due to changes in the CO_2 location; binding modes A and B having CO_2 on opposite sides of the PVAc dimer. Therefore, these two binding modes can be simultaneously populated. This is also true for binding modes C and D. The average

interaction energy for the CO_2/PVAc dimer is -24.3 kJ/mol. This is only slightly more favorable than the CO_2/PLA dimer average binding energy of -22.3 kJ/mol.

Molecular Modeling Discussions: Our calculations indicate that there is little difference in the average interaction energies for the CO_2/PLA dimer and the CO_2/PVAc dimer systems. There is a slight energetic preference for the CO_2/PVAc dimer system, but not enough to account for the observed differences in cloud point pressures for PLA and PVAc shown in Figure 4.7. There are, however, clues to the increased solubility of PVAc relative to PLA. First, the PVAc dimer has considerably more conformational freedom than the PLA dimer and correspondingly more binding modes than the PLA dimer (7 and 3, respectively). This leads to more configurational entropy and more favorable mixing. It is well known that crystalline polymers (with low configurational entropy) generally exhibit poor solubility in CO_2. Second, the PVAc dimer has binding modes that will readily accept multiple CO_2 molecules, whereas the PLA/CO_2 binding modes illustrated in Figure 4.11 can apparently only accommodate a single CO_2 molecule at a time.

4.6 PENDENT SUGAR ACETATE

Many small peracetylated sugars (monosaccharides, disaccacharides, cyclodextrins) exhibit high solubility in CO_2[53, 64]. Although cellulose triacetate (CTA) is composed of peracetylated sugar that constitutes the backbone of the polymer, it is essentially CO_2 insoluble because of its crystallinity. Therefore we decided to evaluate a polymer with a polyethylene backbone and pendent peracetylated sugar groups because it was likely that such a polymer

would not be crystalline. Therefore poly(1-O-(vinyloxy) ethyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside), AcGIcVE was synthesized at Yale following a recently published procedure[70].

4.6.1 Polymerization of AcGIcVE

The polymerization[70] of AcGIcVE was carried out under nitrogen in a dry three neck round bottom flask. AcGIcVE (2.5 mmol, 1.06g) was combined with 10 ml of toluene at 0°C. Then chilled BF_3OEt_2 (0.05mmol) was added to the solution. After stirring the reaction mixture for 24 hrs, polymerization was stopped by adding ammoniacal methanol. The reaction mixture was washed with dilute HCl and then with water. During this washing, some of the polymer precipitated out and some remained in toluene. The precipitates were dissolved in dichloromethane. P(AcGIcVE) was obtained by removing dichloromethane and toluene under vacuum.

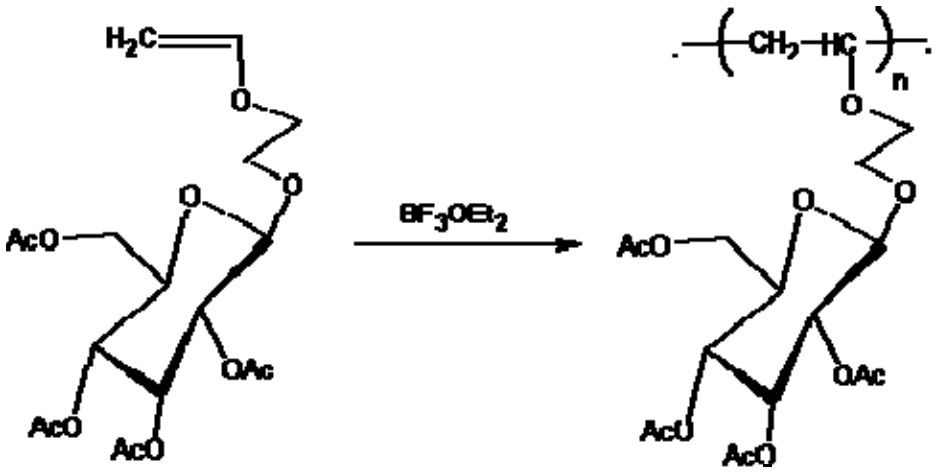


Figure 4.14: Polymerization of AcGIcVE

The polymerization was confirmed by ^1H NMR on Bruker 300 MHz instrument. The NMR spectra were taken in $CDCl_3$ at 298 K which showed that vinyl double bond peak (δ = 6.44

(q, 1H, =CHO)) was absent. The weight average molecular weight was determined by GPC using THF was used as eluent at 298 K and polystyrene standard.

4.6.2 P(AcGIcVE) Phase Behavior

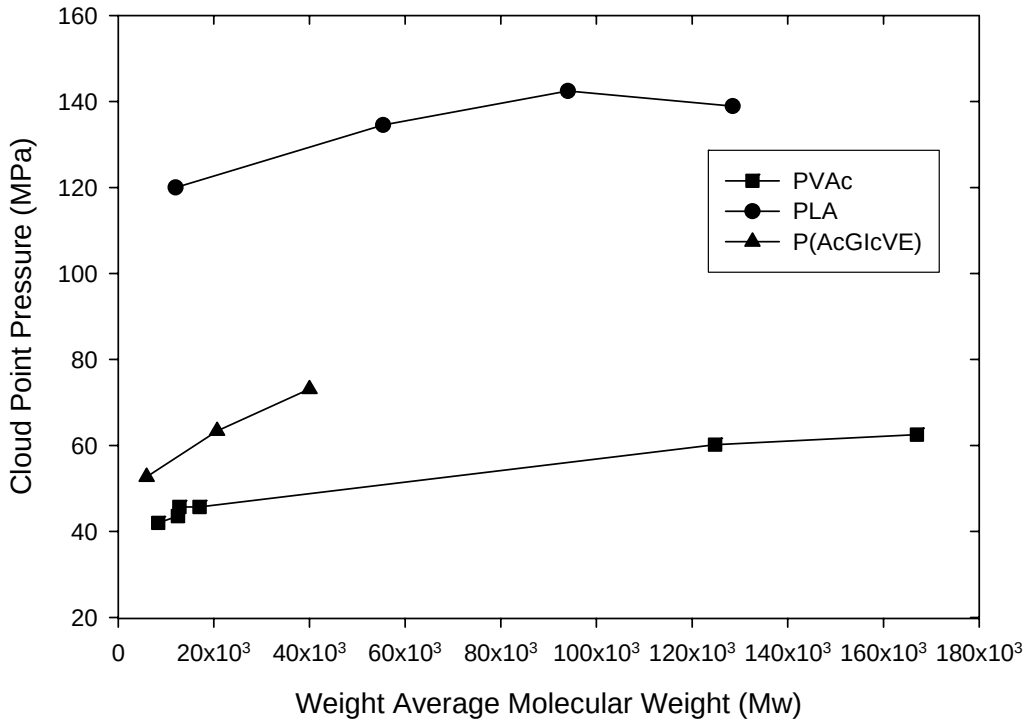


Figure 4.15: Cloud-point pressures at 5 wt% polymer concentration and 298 K for binary mixtures of CO_2 with poly vinyl acetate (■), polylactic acid (●) and P(AcGIcVE) (▲) as a function of weight average molecular weight. Data for Mw = 84500 and 128450 previously published by McHugh. PVAc data previously published[66].

The cloud point pressures for P(AcGIcVE) at 5wt% are also presented in Figure 4.15. These cloud point values are significantly less than those for PLA, but are about 10-20 MPa greater than the cloud point pressures associated with PVAc. It should be noted that the solubility of these polymers in CO_2 was based on polymer molecular weight rather than the number of repeat units because the monomeric unit for P(AcGIcVE) is 418 and contains 4 acetate groups, while

the monomer of PVAc has a molecular weight of 84. Currently, P(AcGIcVE) is the second-most CO_2 soluble, high molecular weight, oxygenated hydrocarbon polymer, second to PVAc.

4.6.3 Comparison of PVAc, P(AcGIcVE) and PLA

It is apparent from the results illustrated in Figure 4.15 that PVAc remains the most CO_2 soluble, high molecular weight, oxygenated hydrocarbon polymer yet identified, followed by P(AcGIcVE) and amorphous PLA. Although the cloud point loci of 5wt% in CO_2 at 298K as a function of molecular weight is relatively flat over a broad range, the differences in pressure between these curves, particularly between PLA and PVAc, is dramatic. One may conjecture that over the molecular weight illustrated in Figure 4.15, PVAc and P(AcGIcVE) (318 - 338 K) relative to PLA (393 – 413K), combined with the more accessible -$OCOCH_3$ pendent groups of PVAc and P(AcGIcVE) rather then the –$OCOCHCH_3$ backbone of PLA account for this difference in miscibility.

4.7 POLY(ACETOXYACETATE)

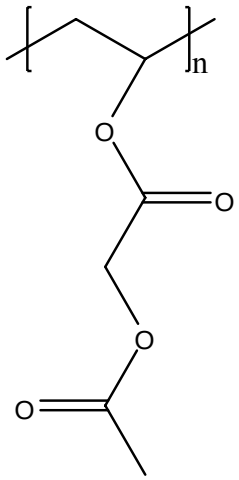


Figure 4.16: Poly acetoxy acetate

Poly (acetoxy acetate) was synthesized by Dr. Chapman's group, in the Department of Chemistry at University of Pittsburgh. It is similar to poly(vinyl acetate), but it has two acetate units in its pendent group, Figure 4.16. These two acetate units were expected to interact with CO_2 better than PVAc and to make the polymer flexible. These polymers were not soluble in CO_2. The lower molecular weight polymer melted in CO_2, but the higher molecular weight sample did not melt; it formed a soft spongy material in CO_2. (This polymer will be evaluated in a 20000 psia cell at Clemson during 2009.)

4.8 BRANCHED POLY VINYL ACETATE

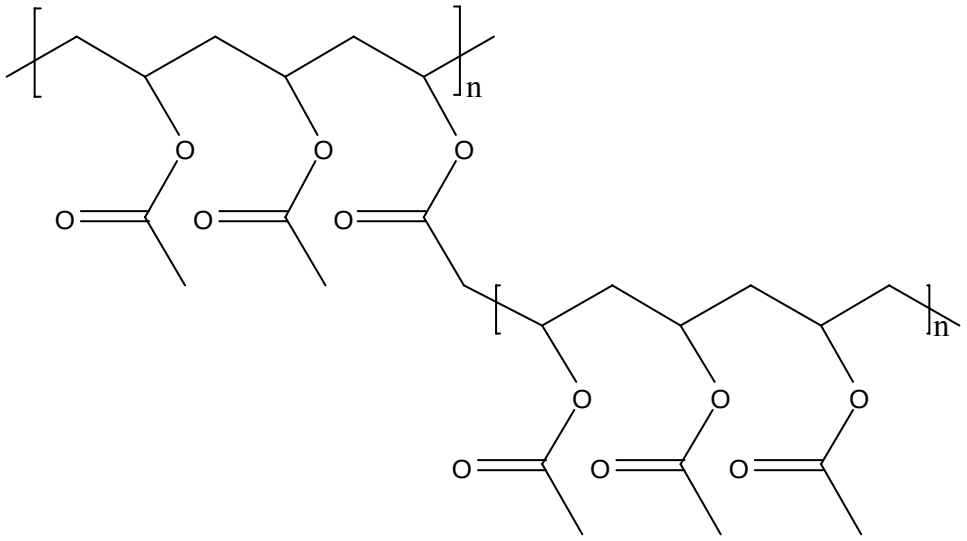


Figure 4.17: Branched poly vinyl acetate

Linear poly vinyl acetate is very CO_2 soluble polymers, however the effect of branching on the solubility of polymer in CO_2 has not been previously studied. In order to make branched polymer, the branching agent, vinyl 2-(ethoxycarbonothioylthio) acetate was synthesized. To a solution of 30 gm potassium ethyl xanthogenate in 600 ml of acetone was added dropwise solution of 20gm vinyl chloroacetate in 70 ml of acetone at 0^oC. The reaction mixture was stirred for 4 hrs at room temperature. Reaction mixture was filtered and acetone was removed using vacuum. Crude product was dissolved in dichloromethane and washed with water. The organic layer was separated and dichloromethane was removed under vacuum. The product was characterized by NMR.

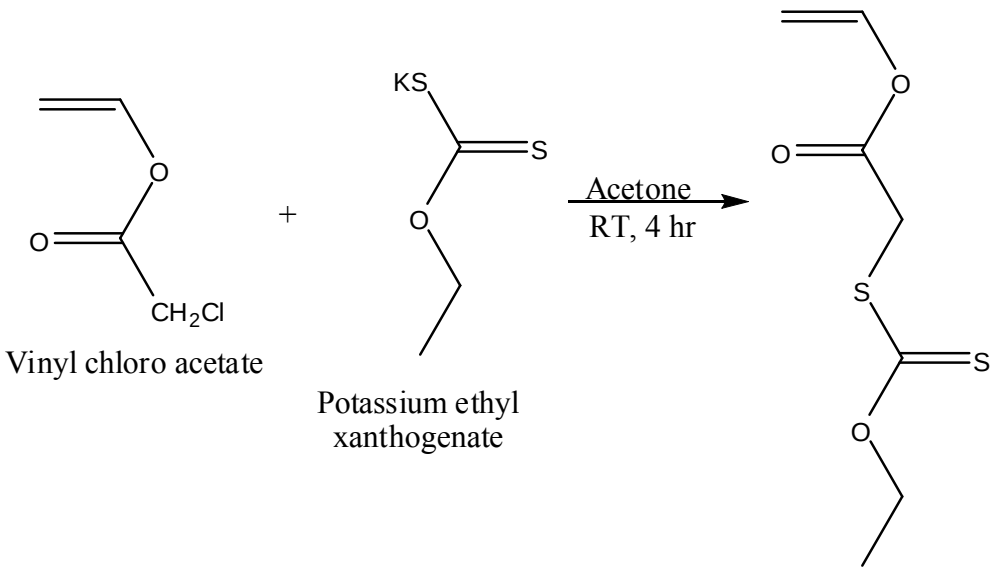


Figure 4.18: Syntheses of branching agent

Branched poly vinyl acetate was synthesized by copolymerization of vinyl acetate and vinyl xanthate(5:1 mole ratio) using AIBN in THF at 50^{o}C for 12 hrs. The product was purified by precipitating it in hexane. It was characterized by NMR and the weight average molecular weight was determined by GPC using THF as eluent at 298 K and polystyrene standard, which was 6000. Branched polyvinyl acetate was not soluble in CO_2, however it melted in CO_2. (This polymer will be evaluated in a 20000 psia cell at Clemson during 2009.)

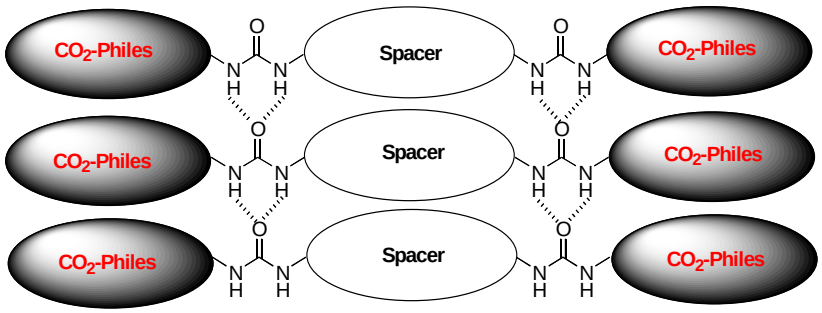
4.9 CONCLUSIONS

Poly(vinyl acetate) remains the most CO_2-soluble, high molecular weight, oxygenated hydrocarbon-based polymer that has yet been identified. Although crystalline, high molecular weight peracetylated polysaccharides such as cellulose triacetate are CO_2 insoluble, we have determined that P(AcGIcVE), a polymer with a polyethylene backbone, a flexible –OCH_2O- spacer and pendent sugar acetates, is more CO_2 soluble that any polymer other than PVAc.

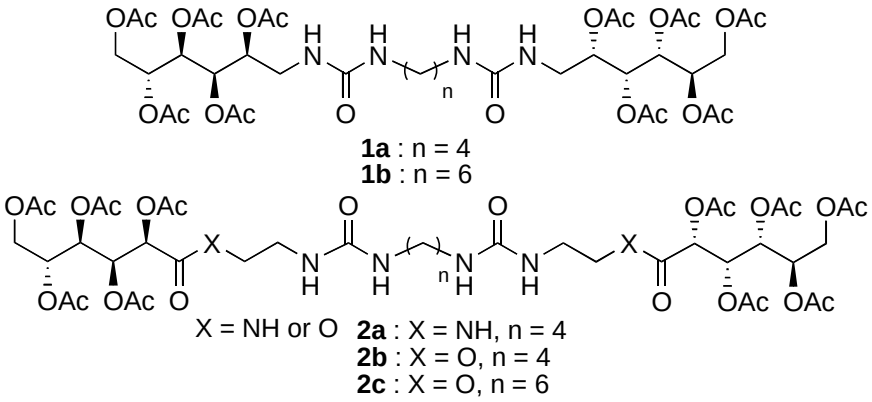
Amorphous PLA requires substantially higher pressures to attain miscibility with CO_2 with PVAc. However, molecular modeling calculations demonstrated that the average interaction energies between CO_2 with dimers of each polymer were comparable in magnitude. These calculations also demonstrated that PVAc has more conformational freedom than PLA and that (unlike PLA) PVAc has binding modes that will accept multiple CO_2 molecules. These may be responsible for the enhanced CO_2 solubility of PVAc.

5.0 HYDROGEN BONDING COMPOUNDS

It has been previously shown that self-aggregating organic compounds containing both hydrogen bonding urea groups and fluorinated CO_2-philic tails could modestly increase the viscosity of $scCO_2$[52]. Upon depressurization these solutions produced free-standing foams which represent organic analogs of silicate aerogels with sub-micron sized fibers and a bulk density reduction of greater than 90% of the parent material[52]. A critical feature of these molecules is the presence of strong and directional hydrogen bonding between carbonyl oxygen and hydrogen in the urea groups within each molecules leading to the formation of two-dimensional sheet like structures. (Figure 5.1a).[71] These molecules can form viscosity enhancing polymeric structures through non-covalent contact in solution, and subsequently free-standing foams upon the removal of the CO_2.



(a)



(b)

Figure 5.1: (a) Intermolecular hydrogen bonded network of bis-ureas with CO_2-philes (b) Bis-ureas with two highly acetylated arms

The objective of the present work was to design non-fluorous hydrogen-binding derivatives capable of dissolving in CO_2. An inexpensive and readily available source of multiple hydroxyl groups is the family of mono-, di- and oligosaccharides. These can be readily converted into their peracetylated derivatives, which should have a similar density of electronegative groups to perfluoroalkanes. In particular, gluconic acid is readily available from glucose by oxidation and should be easily converted into its peracetylated derivative. Thus, peracetylated gluconic acid was chosen as the candidate for the non-fluorous CO_2-phililic appendage and commercially available D-glucamine was also chosen for easy access to the bis-urea family (Figure 5.1b).

5.1 SYNTHESIS OF BIS-UREA COMPOUNDS

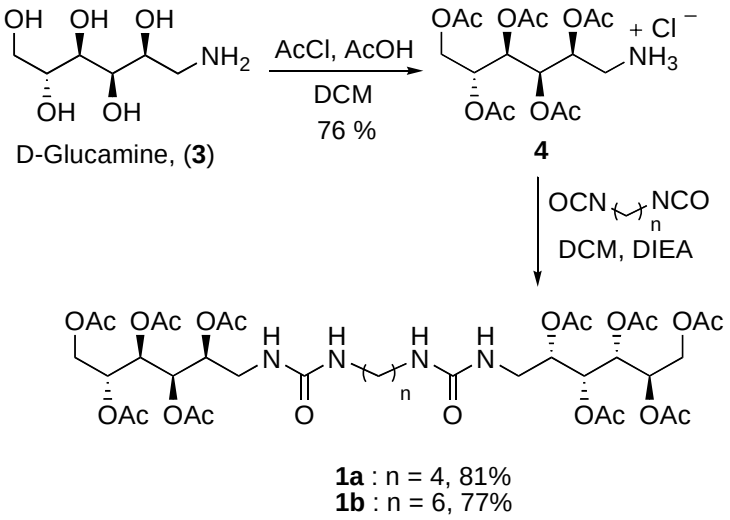


Figure 5.2: Synthesis of bis-ureas 1a and 1b

The synthesis of bis-urea 1 begins with the per-acetylation of commercially available D-glucamine (3). In contrast to the longer four step synthesis of acetylated glucamine, 4, reported by Hoeg-Jensen et. al.[72], we could selectively acetylate hydroxyl groups in glucamine with acetyl chloride under acidic conditions[73] directly. Penta-acetylated D-glucamine salt, which was easily purified through re-crystallization, reacted with various commercially available alkyl bis-isocyanates at room temperature to give the desired bis-ureas 1 in high yield (Figure 5.2). The CO_2-philic acetylated sugars are located adjacent to the bis-urea functionality in bis-ureas 1, and sterically hinder the formation of hydrogen bonded networks as in Figure 5.1a. An alternative design (shown in 2) places the peracetylgluconate groups more distant from the ureas through the insertion of ethanolamine or ethylenediamine spacers. Esters and amides of gluconic acid, 8, were synthesized by using a dehydrating agent such as the 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC hydrochloride). After deprotection of the Boc-protected

esters or amides in situ, the resulting free amines were reacted with bis-isocyanates to form the desired bis-ureas 2 in moderate to high yields (Figure 5.3).

The simplicity of this approach made it readily applicable to branched species, containing multiple acetylated gluconate groups. Cooper et. al. have previously shown that the fourth generation hydrophilic dendrimer, DAB-dendr-(NH2)32, functionalized with CO_2-philic per-fluoropolyether chains is highly CO_2 soluble. A similar, albeit more limited approach could be taken to the dissolution of self-assembling bis-urea dendrimer in $scCO_2$ through the attachment of multiple CO_2-phlic groups, as in 10. The Boc-protected bis-ester amine, 9 was synthesized from the reaction of two equivalents of peracetylated gluconic acid with Boc-protected serinol. This was converted using the same reaction conditions, as in the synthesis of 1 and 2 to afford the bis-urea derivative with four CO_2-philic groups, 10. The yield was highly affected by the concentration of the reaction mixture. In order to avoid intramolecular side reactions and promote intermolecular reaction, the reaction was conducted at high concentration and resulted in the dendrimeric bis-urea in a moderate yield.

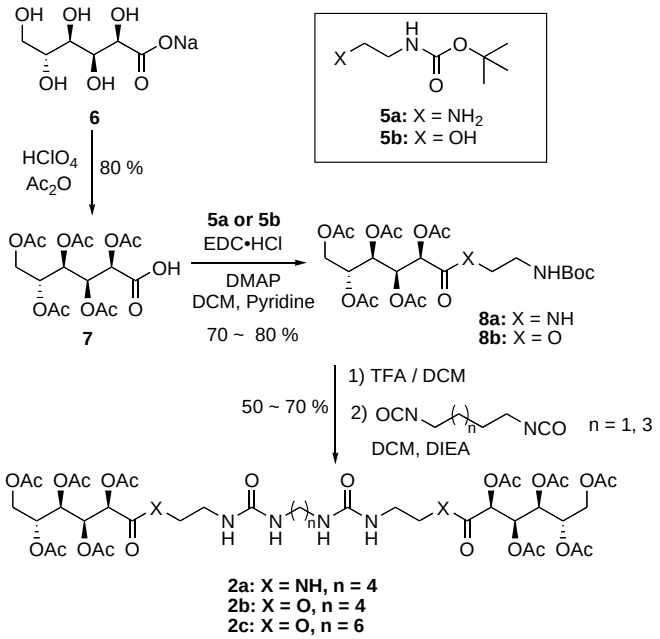


Figure 5.3: Synthesis of bis-ureas 2a, 2b, and 2c.

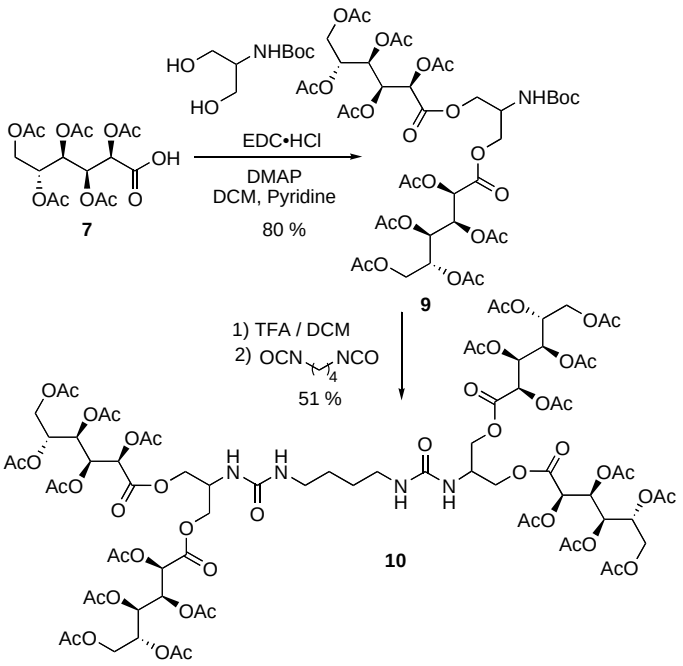


Figure 5.4: Synthesis of dendrimer 10

5.2 PHASE BEHAVIOR

At ambient temperature, bis-ureas 1a and 1b were not soluble in $scCO_2$ even at pressures up to the limit of the instrument (68.95 MPa) or when heated to 100°C. Chain length (butane vs. hexane spacer) did not have any effect on the solubility of these compounds in $scCO_2$. It is possible that the close proximity of the acetates to the urea groups may inhibit both the insolvation by CO_2 as well as the inaggregation through hydrogen bondings.

Bis-ureas 2a - 2c containing an ethylene spacer between the CO_2-philic peracetates and the bis-urea groups were synthesized to test the effect of distance between the core and the tail in these molecules. Bis-urea 2a did not dissolve into CO_2 at any temperature and pressure, possibly due to the CO_2-phobic nature of the amide group installed as a linkage. However, replacement of the amide by ester groups gave an oxygen rich and more CO_2-philic series in bis-ureas 2b

(5R,6R,7S,8R,27R,28S,29R,30R)-5,6,7-triacetoxy-2,9,14,21,26-pentaoxo-3,10,25-trioxa-13,15,20,22-tetraazahentriacontane-8,27,28,29,30,31-butylhexaacetate) and 2c (5R,6R,7S,8R,27R,28S,29R,30R)-5,6,7-triacetoxy-2,9,14,21,26-pentaoxo-3,10,25-trioxa-13,15,20,22-tetraazahentriacon-tane- 8,27,28,29,30,31-hexaylhexaacetate) ((Figure 5.3). At 298 K, these highly acetylated bis-ureas dissolved in CO_2 at pressures of 62 MPa at 1 wt % for 2b and 65 MPa at 1 wt % for 2c. The single phase, transparent solution attained under these conditions (e.g. 62 MPa, 298 K, 1 wt% of compound 2b) was apparently meta-stable. After 2-5 minutes, A light suspension of fine fibers began to form in the solution. Apparently, at isothermal and isobaric conditions, the dissolved compound slowly aggregated due to hydrogen bonding and the macromolecule precipitated, resulting in the formation of fibers. Within 20 minutes, the sample volume was filled with fibers and upon the removal of CO_2, very brittle, freestanding, micro-fibrillar foam formed, with an average fiber diameter of 1 - 3 microns. In the phase behavior studies at lower (286 K) and higher (310.5 K) temperature and a pressure of 65 MPa for bis-urea 2b, a single transparent phase was never attained. Nonetheless, the powdery compound initially charged into the cell dissolved and then precipitated in the form of fibers. This compound appeared to be changing in morphology from a powder to fibers at isothermal, isobaric conditions.

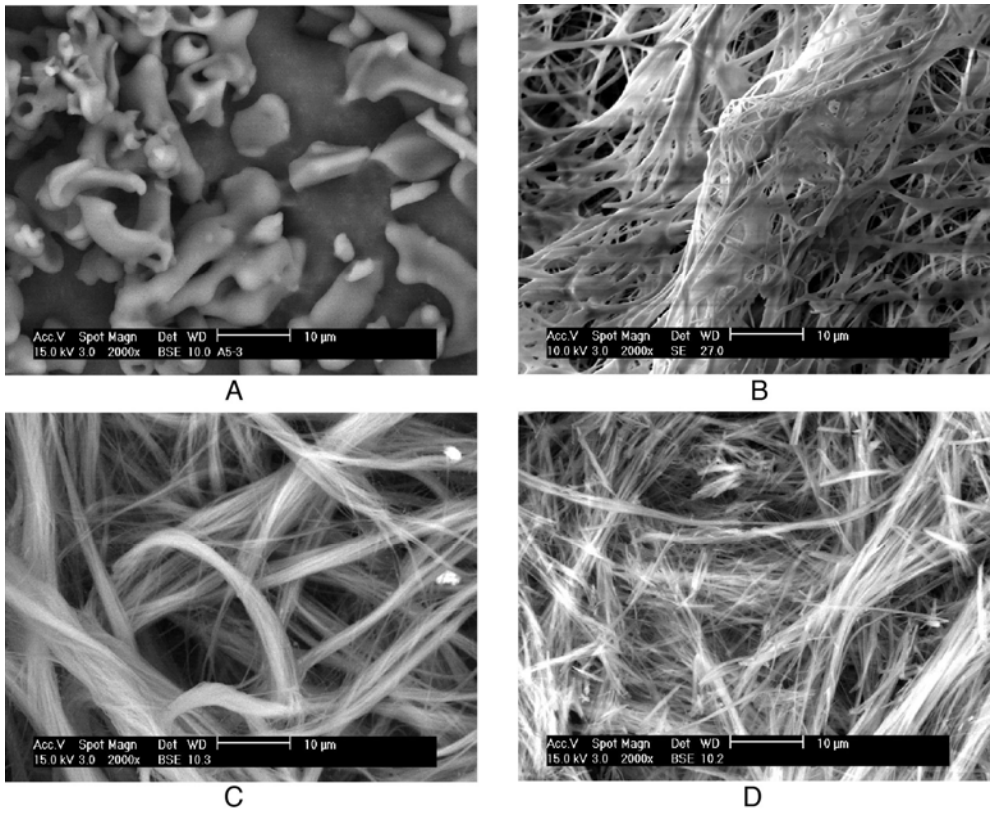


Figure 5.5: SEM images of compound 2b before introduction of CO_2 (A), and the fibers formed at pressure at 13°C (B), 25°C (C) and 37.5°C (D)

SEM images of all the fibrous material obtained at different temperatures are shown in Figures 5.5 B-D and the morphology of the powder sample before mixing with CO_2 is shown in Figure 5.5 A. At low temperature, compound 2b produced foam with a highly interconnected micro-fibrillar structure with fiber diameters less than 1 micron (Figure 5.5 B). The foam produced from compound 2b at ambient temperature has a major fiber diameter of 1 - 3 microns, which is composed of sub-micron fibers, and had higher porosity than that formed at low temperature (Figure 5.5 C). The foam produced at 37.5°C was very brittle and had a fiber diameter around 1 micron (Figure 5.5 D).

The improvements in CO_2 solubility seen in 2b and 2c encouraged us to prepare, a first generation dendrimer 10,((5R,6R,7S,8R,27S,28R,29S,30S)-5,6,7,8-tetraacetoxy-2,9,14,21,26-pentaoxo-12-(((2R,3S,4S,5R)-2,3,4,5,6-pentaacetoxy-hexanoyloxy)methyl)-23-(((2S,3R,4S,5S)-2,3,4,5,6-pentaacetoxy-hexanoyloxy)methyl)-3,10,25-trioxa-13,15,20,22-tetraazahentriacontane-27,28,29,30,31-pentaylpentaacetate) containing four CO_2-philic peracetylated groups around a bis-urea core, shown in Figure 5.4. In contrast to the bis-ureas 2b or 2c (1% dissolution at 62 or 65 MPa), simple dendrimer 10 was more readily dissolved in CO_2 at a notably lower pressure of 27 MPa at 1 wt%. Compound 10 dissolved in the range of 1 - 5 wt % in liquid CO_2 at 298 K as well as in supercritical CO_2 at 317 K. These are the first CO_2 soluble dendrimers composed solely of C, O, H and N. Unlike the linear, bis-ureas 2b or 2c discussed earlier, this dendrimer 10 formed a powder, not a rigid foam, upon the removal of CO_2. Both trends indicate that hydrogen bonding did *not* act to associate the dendrimers in solution,

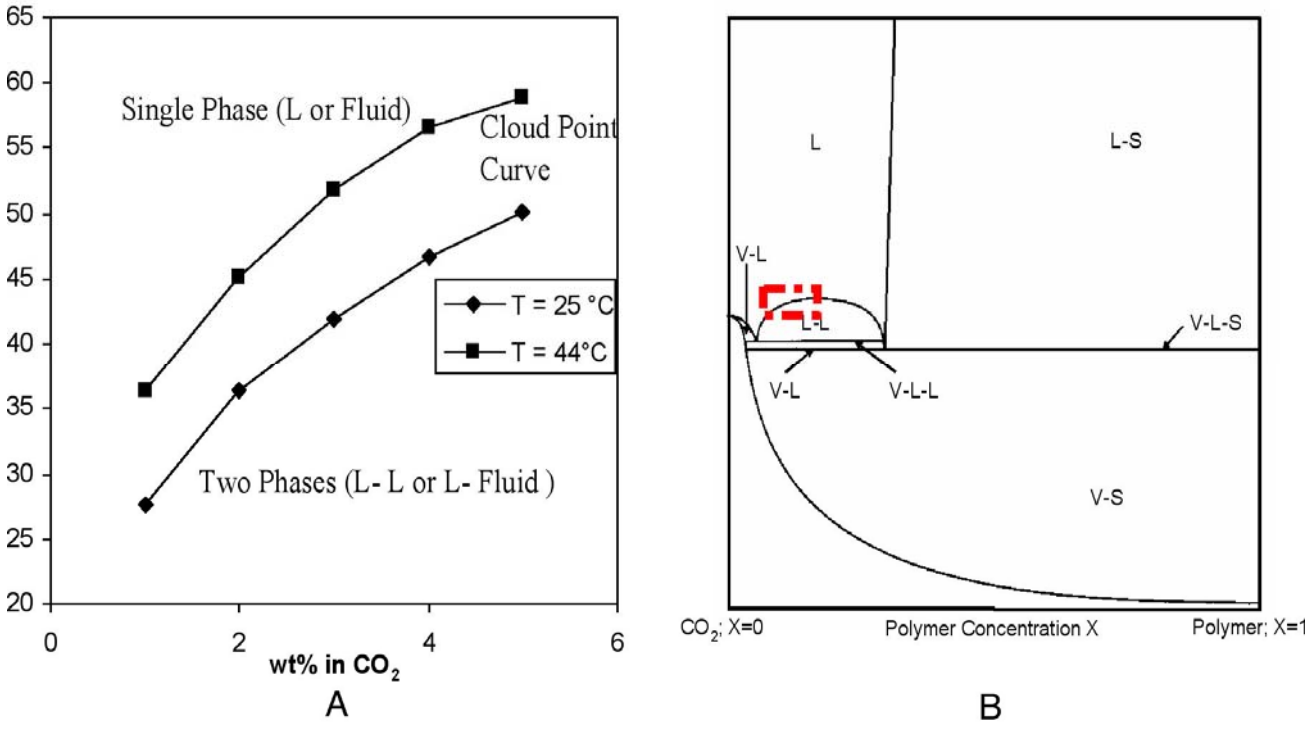


Figure 5.6: Cloud point curve of dendrimer in CO_2 at different temperature (A) General P-x isotherm of binary mixture in CO_2 (B).

5.3 CONCLUSION

In conclusion, a non-fluorous CO_2-philic compound with a core of two ureas separated by a short alkyl chain and two highly oxygenated "arms" derived from per-acetylated gluconic acid was dissolved to 1wt % in supercritical CO_2 at 298 K and 65 MPa. Upon dissolution, formation of micro-fibrillar foam with fiber diameters of approximately 1-3 microns was observed and this brittle networked material retained its integrity upon depressurization of the CO_2. A non-fluorous, first-generation highly CO_2-soluble dendrimer with four per-acetylated "arms" derived from acetylated gluconic acid and a bis-urea core was also synthesized. This dendrimer was

soluble up to 5wt% in liquid and supercritical CO_2. The phase behavior of the dendrimer 12 in CO_2 is presented in Figure 5.6 in the form of a P-x isotherm. These results constitute a small portion of the overall phase Px diagram of this binary mixture, which is illustrated in Figure 5.6 B. The small box within this figure represents the measured phase behavior shown in Figure 5.6 A. These results indicate that acetylation provides an environmentally benign pathway to the generation of small, non-fluorous CO_2-soluble hydrogen-bonding compounds and dendrimers.

The bis urea compound was not even assessed as a thickener because a stable transparent solution could not be achieved. The dendrimer was not assessed as a thickener because the lack of any fiber formation upon depressurization implied that associations were not occurring in solution.

6.0 DESIGN OF CO_2 THICKENER

CO_2 soluble polymers, alone, cannot be used to increase the viscosity of CO_2 because (unlike water) ultra-high molecular weight polymers of any composition cannot, to the best of our understanding, dissolve in CO_2. Although significant viscosity increase may be attained using ultra-high molecular weight homopolymers, it is quite unlikely that a polymer with molecular weight of 1-10 million could dissolve in CO_2 at pressures less than minimum miscibility pressure, which is roughly 10 MPa at 295K.

Therefore first step in making a successful CO_2 thickener is to identify a CO_2-philic monomer based on oligomeric and/or polymeric phase behavior results. Then the CO_2-philic monomer can be copolymerized with a CO_2-phobic monomer which has the capacity to induce intermolecular associations such that when the copolymer is dissolved in CO_2, it can promote association among polymer chains. Alternately a copolymer consisting of the CO_2-philic monomer and a CO_2-phobic monomer can be purchased and transformed via replacement of the CO_2-phobic group (e.g. hydroxyl) with a more appropriate associating group.

To date only single CO_2 thickener has been identified, a random copolymer of **f**luoro**a**crylate and **st**yrene, dubbed. polyFAST, developed by Enick, Beckman and coworkers[50]. The increase in viscosity was due to π-π stacking of aromatic side chain functional groups. The optimum composition of the copolymer was found to be 29 mol% styrene and 71 mol% fluoroacrylate. Addition of 1.2 wt% of the copolymer increased the viscosity of CO_2 by the

factor of 19 relative to neat CO_2 as determined at a superficial velocity of 0.00035 cm/s sandstone core.

6.1 STYRENE ASSOCIATION

It has been well known that the aromatic rings, for example benzene, associate via electrostatic, non bonding interactions which results into stacking of these rings[74, 75]. This stacking is due to: -

- Delocalization of electrons in the pi orbital of benzene which creates a negative charge in a plane above and below the ring.
- Slight positive charge on the hydrogen atoms at the end of ring.

Due to this charge distribution, the hydrogen atoms of one ring are attracted towards the electron rich region above the other benzene ring, resulting in the stacking of benzene rings shown in Figure 6.1[76, 77]. Since benzene is non-polar and have zero dipole, these electrostatic interactions are attributed to their quadrupole –quadrupole interactions[78, 79] [63, 64]

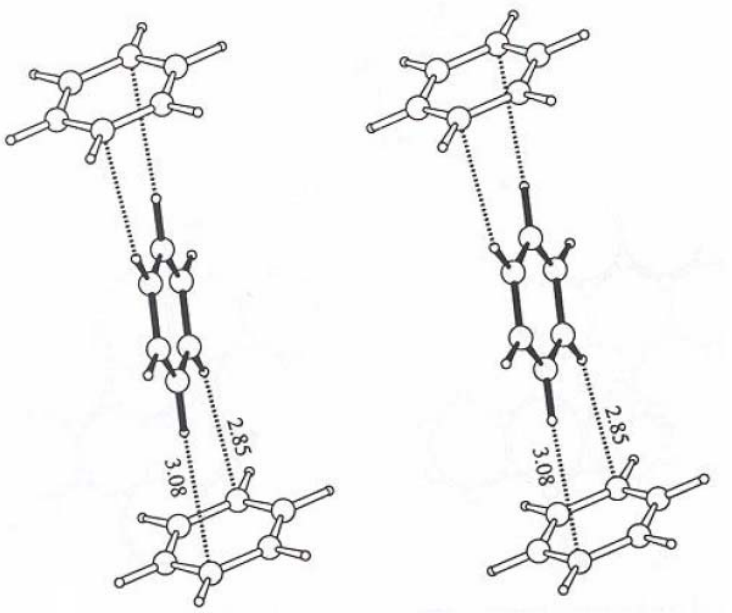


Figure 6.1: Stacking of benzene ring

This quadrupole - quadrupole interaction between the pendant phenyl groups of the (fluoroalkyl acrylate-co-styrene) polymer resulted in the individual copolymers not only dissolving in CO_2, but also interacting to form extremely high molecular weight viscosity-enhancing macromolecular structures.

6.2 STRATEGY OF MAKING A CO_2 THICKENER

The objective of this research is to make a CO_2 thickener only from carbon, hydrogen and oxygen. Therefore *vinyl acetate*, the monomer of the most CO_2-soluble oxygenated hydrocarbon polymer, poly(vinyl acetate) (PVAc), was selected as the CO_2-philic group. It is recognized that this PVAc-based copolymer will *not* be able to be used in the field because the pressure required to dissolve PVAc in CO_2 is much greater than the MMP of CO_2 EOR projects, and the inclusion of the CO_2-phobic associating groups will only serve to diminish its solubility in CO_2.

Nonetheless, PVAc remains the most CO_2 philic nonflurous hydrocarbon based polymer, and the copolymer derived from this compound will be used to demonstrate that a non-fluorous co-polymeric thickener can be designed for CO_2, albeit the pressure required for dissolution is too high for practical application.

The second step is the selection of an appropriate self associating monomer which can be co-polymerize with vinyl acetate. Styrene was successfully used in making fluorinated CO_2 thickener. As styrene is somewhat CO_2-phobic, the CO_2-solubility of co-polymeric thickener that includes styrene is expected to be less than the CO_2-philic homopolymer. Although styrene was successfully employed in the synthesis of polyFAST, styrene *cannot* be used for making copolymer with vinyl acetate because there is a large difference in there reactivity ratio (VAc = 0.001, Styrene = 42). Therefore simple radical copolymerization will give a mixture of homopolymers rather than random copolymers.

The following monomers, each of which contains a pendant aromatic group, were considered for copolymerization with vinyl acetate.

6.3 ASSOCIATING GROUPS

6.3.1 Vinyl Benzoate

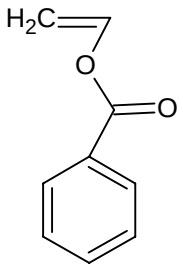


Figure 6.2: Vinyl benzoate

As we know that PVAc is the most CO_2 soluble non-fluorous high molecular weight polymer, a methyl group at the end of side chain was replaced with benzene group to make a monomer that may be able to generate copolymers with VAc.

Material: Poly(vinyl alcohol) 78% hydrolyzed was bought from polymer science. Pyridine, benzoyl chloride and tetrahydrofuran was bought from Aldrich and used without purification.

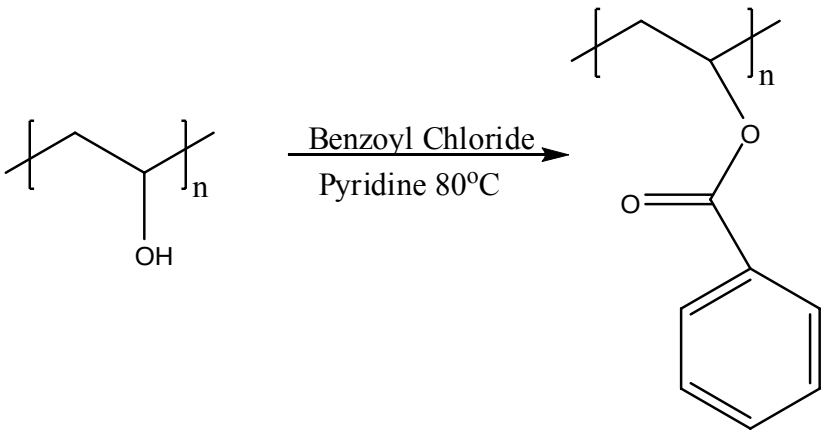


Figure 6.3: Synthesis of Poly (vinyl benzoate)

Synthesis of Poly (vinyl benzoate): The reaction was carried under nitrogen atmosphere in a three neck round bottom flask. The mixture of pyridine(0.2 mol) and poly(vinyl alcohol) (0.035mol) was heated at 80°C for 12 hrs. Poly(vinyl alcohol) did not dissolved in pyridine After 12 hrs a solution of benzoyl chloride (0.045 mol) and pyridine (0.1 mol) was added to the reaction mixture drop wise at 60°C and the reaction was monitored by IR (disappearance of C-OH band). Poly(vinyl benzoate) was obtained by precipitating the reaction solution in excess of water. Polymer was dissolved in tetrahydrofuran and re-precipitated in water for further purification.

Result: Poly (vinyl benzoate) of 6000 molecular weight was synthesized and tested for CO_2 solubility. It melted in CO_2 but was not soluble at 298 K and 70 MPa. The insolubility of this homopolymer was not surprising. However the melting point depression is a favorable indication that this monomer is more CO_2-philic than styrene.

6.3.2 Benzyl vinyl carbonate

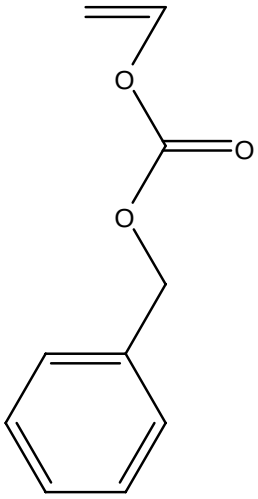


Figure 6.4: Benzyl vinyl carbonate

Its molecular structure is very similar to vinyl benzoate. In this monomer, the benzene ring is further away from the main chain by CO_2 philic -OCH_2- group. The additional CO_2 philic group should make this monomer more CO_2 philic. Homopolymer of benzyl vinyl formate was not synthesized.

6.3.3 4-acetoxystyrene

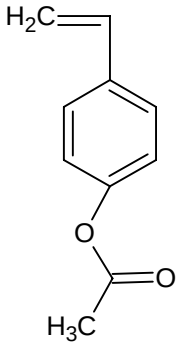


Figure 6.5: 4-acetoxystyrene

In order to increase the likelihood that VAc could copolymerize with a monomer containing an aromatic ring the structure of styrene monomer is modified by adding a CO_2-philic acetate group to the benzene ring. Poly (4-acetoxy styrene) of 32000 weight average molecular weight was purchased from polymer source and was tested for it CO_2 solubility. It melted and become sticky in CO_2 but was not soluble up to 70 MPa at room temperature. The insolubility of this homopolymer was not surprising. However the melting point depression is a favorable indication that this monomer is more CO_2-philic than styrene because polystyrene neither melts nor dissolves in dense CO_2.

6.4 SYNTHESIS OF CO-POLYMERIC THICKENERS

Usually the copolymers are made by the polymerization of two monomers in the presence of initiator. However, it was easier in this case to modified the functional groups on the commercially available vinyl acetate-vinyl alcohol co-polymers to our requirements. All the chemicals were from Sigma-Aldrich.

6.4.1 Synthesis of poly (vinyl acetate-co-benzoyl) copolymer

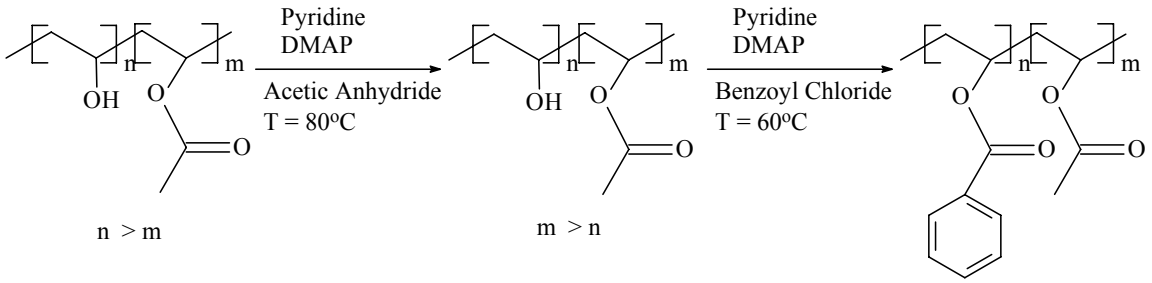


Figure 6.6: a) Poly (vinyl alcohol) 80% hydrolyzed, b) Poly (vinyl acetate-co-vinyl alcohol) with 80% acetate groups, c) Poly (vinyl acetate-co-benzoyl)

This copolymer is made in two steps.

Step I: Making poly(vinyl acetate-co-vinyl alcohol) with 80 %acetate and 20 % alcohol groups: - Poly (vinyl alcohol) (10 gm, 6000 Mw, 80 % hydrolyzed) was dispersed in 80 ml of pyridine at 80°C. After 4 hr, acetic anhydride (16 ml, 50% excess) was added to the reaction mixture. Poly (vinyl alcohol) started to dissolve in pyridine as it acetylated. The reaction was run overnight at 80°C. Poly (vinyl acetate-co-vinyl alcohol), 20 % hydrolyzed, was obtained by precipitating the reaction mixture in water. The copolymer was further purified by dissolving it in THF and again precipitating in water. NMR showed that the polymer has about 80% acetate groups.

Step II: Adding benzene functionalized group to make thickener: - Above copolymer was dissolved in toluene. After adding pyridine, DMAP, and benzoyl chloride, the reaction mixture was stirred for 4 hr at 80°C. After that more pyridine, DMAP and acetic anhydride were added and the reaction was stirred at 80°C overnight. Polymer was obtained by precipitating the reaction mixture in water. It was further purified by dissolving it in THF and again precipitating

in water. NMR showed the polymer has about 5 % benzene functional group. Copolymer with 10% benzene functional group was also synthesized.

6.4.2 Synthesis of poly (vinyl acetate-co-benzyl vinyl carbonate) copolymer

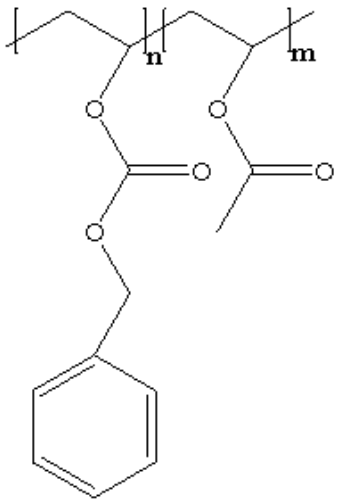


Figure 6.7: Poly (vinyl acetate co benzyl vinyl carbonate)

The benzyl formate group is very similar to benzoyl group with the addition of $–OCH_2$ group in the side chain. Lengthening of the side chain will make copolymers more flexible and addition of oxygen will provide more sites for CO_2-polymer interactions. The same synthesis strategy that used for poly (vinyl acetate-co- benzoyl) was used to make this copolymer. Chloro benzylformate was used instead of benzoyl chloride to put aromatic group on the copolymer. Copolymer with 5% benzyl vinyl carbonate group was synthesized and characterized by NMR.

6.5 PHASE BEHAVIOR

The phase behavior curve for these copolymers in CO_2 is shown in Figure 6.8. Poly (vinyl acetate-co-benzoyl) with 5% benzoyl group was soluble in CO_2 at 64 MPa at 3wt %. The pressure required to dissolve PVAc, of 11000 Mw and 5wt%, is around 40 MPa. As expected, the solubility of copolymer in CO_2 is decreased substantially on addition of aromatic groups. Poly (vinyl acetate-co- benzoyl) with 10% benzoyl group was not soluble in CO_2. Poly (vinyl acetate-co-benzyl vinyl carbonate) was soluble in CO_2 for only 0.5wt% at 63MPa. As expected, this pressure range greatly exceeds the MMP value.

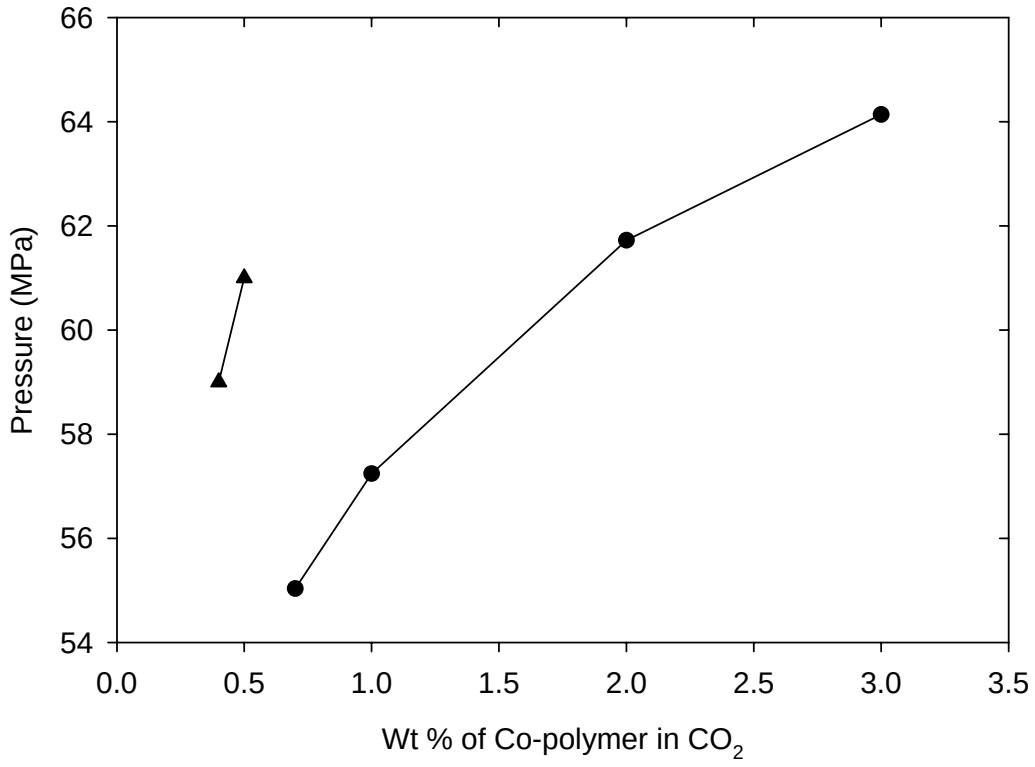


Figure 6.8: Phase behavior of co-polymeric thickeners, Poly (vinyl acetate-co-benzoyl) (●) and Poly (vinyl acetate-co-benzyl vinyl carbonate) (▲).

6.6 VISCOSITY MEASUREMENT

6.6.1 Experimental setup

Falling cylinder viscometry was used to measure the relative viscosity of the co-polymeric thickener. The equipment used for phase behavior measurements (described in section 5.6).was used for this purpose. An aluminum cylinder with very smooth surfaces, height of 1 in and diameter of 1.245 in was used. This cylinder was put in the glass cell along with polymer and the system was pressurized and stirred until single phase was obtained. Once single phase is obtained stirring is stopped and cell is inverted and time taken by the cylinder to fall a certain distance is measured, Figure 6.9. First few centimeters of the falling cylinder are ignored to make sure that cylinder has reached its terminal velocity. This procedure is repeated about 10 times to get consistent reading. The same experiment is also done for neat CO_2.

The relation between the velocity of falling cylinder and viscosity of the fluid is derived from Navier-Stokes equation which has following assumptions:

- The cylinder and glass tube are always coaxial and concentric.
- The compressibility of fluid is low during the experiment.
- Density difference of the fluid above and below the piston is negligible
- Temperature and pressure are maintained constant during the experiment

The governing equation for the system is:

$$\eta = \kappa \frac{(\rho_c - \rho_f)}{V_t} \qquad \textbf{Equation 6.1}$$

where η is the viscosity of fluid, ρ_c and ρ_f are the density of cylinder and fluid, V_t is the terminal velocity of the falling cylinder and κ is the viscometer constant which is determined by

calibration by a fluid of known density and viscosity. Equation 6.1 stands good for Newtonian fluids but it can be used for non Newtonian fluids if shear rates are low and dependence of viscosity on shear is not considered. Comparison of viscosity of thickener added CO_2 and neat CO_2 gives us:

$$\frac{\eta_{solution}}{\eta_{CO_2}} = \frac{V_{CO_2}}{V_{solution}} = \frac{t_{solution}}{t_{CO_2}} \qquad \textbf{Equation 6.2}$$

where $t_{solution}$ and t_{CO2} are the time taken by the cylinder to fall a particular distance through CO_2. Equation 6.2 gives us relative increase in the viscosity of CO_2 when thickener is added.

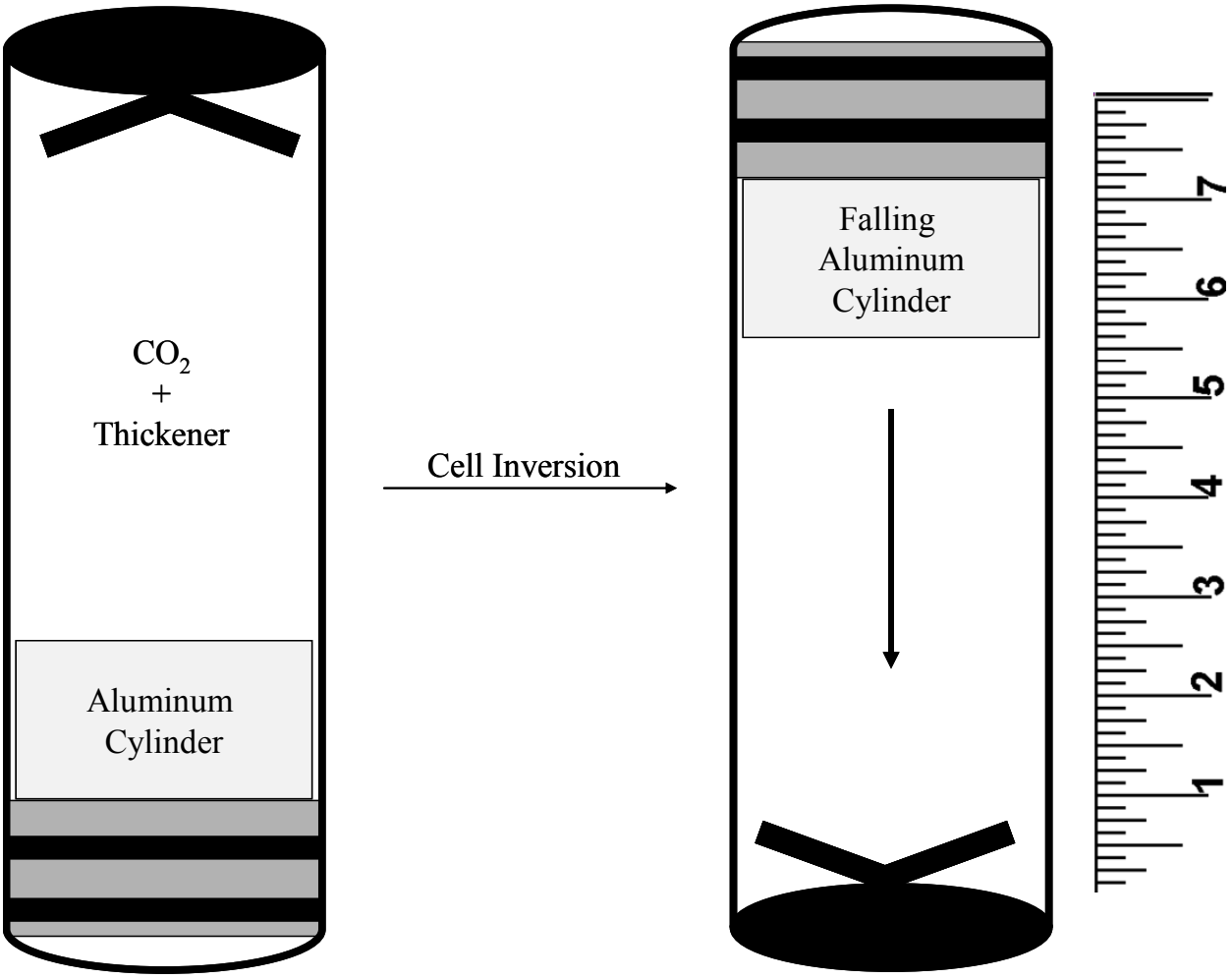


Figure 6.9: Viscosity measurement appartus

6.6.2 Viscosity measurement results

Falling cylinder test were performed for Poly (vinyl acetate-co-benzoyl) and CO_2 solution for 2wt% and 1wt% at 25^oC and 64 MPa. As a control terminal velocity of CO_2 and poly (vinyl acetate), homopolymer, is measured at 25^oC and 63 MPa. No apparent decrease in the terminal velocity of aluminum cylinder was observed. Average terminal velocity of falling cylinder in pure CO_2 was 0.649 cm/s and in 2 wt% PVAc solution in CO_2 was 0.0679 cm/s. However substantial decrease in the terminal velocity was observed for 2 wt% of Poly (vinyl acetate-co-benzoyl) in CO_2 which was 0.0402 cm/s. As expected, average terminal velocity increased to 0.0478 cm/s when the 1 wt% of poly (vinyl acetate-co-benzoyl) was used, but it was still less then pure CO_2. This result indicates that benzene ring associates to generate intermolecular associations and produce a thickening effect.

Using equation 6.2 relative viscosity of the co-polymeric solution was calculated and the comparison of relative viscosity increase for 2wt% and 1wt%. The relative viscosity of CO_2 increased by roughly 40% at a copolymer concentration of 1wt% and 80% at 2wt% at shear rates of 6200 $s^{-1}$and 5080 s^{-1} respectively. This is the first documented non-fluorous CO_2 thickener. Unfortunately, the pressure required to dissolve this thickener in CO_2 far exceeds the MMP.

7.0 SUMMARY AND CONCLUSIONS

7.1 POLYMERS

Several acetate-rich oxygenated hydrocarbon polymers were designed in hopes of identifying a polymer more CO_2-soluble than poly(vinyl acetate). Three polymers that were analogous to PVAc were considered. Poly(vinyl propionate) had a side chain with one additional methylene group between the carbonyl carbon and the methyl group at the end of side chain, as compared to PVAc. It was postulated that this could have made this polymer more flexible and the acetate group more accessible to the dense CO_2. Poly(acetoxyacetate) possessed two acetate groups in each side chain rather and it was thought that the increased number of interactions between CO_2 and the acetate could have increased the solubility of the polymer. A branched poly(vinyl acetate) (rather than the linear PVAc) was also synthesized. None of these polymers dissolved at pressures up to 69MPa (the pressure limit of the University of Pittsburgh phase behavior cell), however each one melted and swelled; indicators that dissolution may occur at slightly higher pressures.

Acetylated sugars, such as glucose pentaacetate and galactose pentaacetate have been previously established as extraordinarily CO_2-soluble small compounds. In an attempt to develop a non-crystalline polymer rich in sugar acetates, a polymer was designed with a polyethylene backbone and pendant sugar acetate groups. This polymer, poly (1-O-

(vinyloxy)ethyl - 2,3,4,6 – tetra –O – acetyl – β – D - glucopyranoside), P(AcGIcVE), was demonstrated to be the second most CO_2 soluble oxygenated hydrocarbon polymer yet identified. P(AcGIcVE) is 5wt% soluble in CO_2 at pressures about 20-25 MPa higher than PVAc of comparable molecular weight at 298 K.

It had been previously established that very high molecular weight amorphous poly(lactic acid) was soluble in CO_2 at a pressure greater than that of PVAc. In this study, a broad range of amorphous PLA was assessed, and it was determined that PLA is the third most CO_2 soluble polymer, exhibiting 5wt% polymer cloud point pressures about 60-70 MPa greater than that of PVAc of comparable molecular weight at 298 K.

Polyvinyl acetate remains the most CO_2-soluble high molecular weight oxygenated hydrocarbon polymer.

7.2 CO-POLYMERIC THICKENER

Poly(vinyl acetate) was selected as the base polymer for the design of a non-fluorous CO_2 copolymeric thickener. In our group's prior research, the only effective CO_2 thickener ever identified was a fluoroacrylate-styrene copolymer. The fluoroacrylate provided CO_2-philicity while the styrene facilitated viscosity-enhancing intermolecular associations via π-π stacking. Therefore, in this work, a copolymeric thickener was designed containing vinyl acetate for CO_2-solubility and a pendant phenyl group for intermolecular associations. Styrene cannot be co-polymerized with vinyl acetate because of large difference in reactivity ratios. Therefore a vinyl acetate-vinyl alcohol co-polymer was reacted with either benzoyl chloride or chloro benzylformate. For both copolymers, the copolymer solubility decreased as the CO_2-phobic

aromatic group content increased. Promising results were obtained with poly(vinyl acetate-co-vinyl benzoate$_{5\%}$). The viscosity of CO_2 increased by roughly 40% at a copolymer concentration of 1wt% and 80% at 2wt% at shear rates of 6200-5080 s^{-1} respectively at 298 K. Therefore poly(vinyl acetate-co-vinyl benzoate$_{5\%}$) is the first documented non-fluorous CO_2 thickener capable of increasing the CO_2 viscosity substantially at dilute concentrations of ~1wt%. Unfortunately, the pressure required to dissolve this copolymer in CO_2 at 298 K (~9000-10000 psia change to MPa) greatly exceeds the MMP of CO_2 floods at the same temperature (1200-1800 psia change toMPa). Because we were not able to identify a hydrocarbon-based polymer more CO_2-philic than PVAc, it is doubtful that a non-fluorous, copolymeric thickener capable of dissolving in CO_2 at practical EOR pressure conditions can be identified.

The only other non-fluorous polymer known to be more CO_2-soluble than PVAc is polydimethyl siloxane, PDMS. Therefore, we evaluated three commercially available PDMS polymer with 8-12% substitution of a pendant phenyl group. Two PDMS-based copolymers, (~10% phenyl methyl siloxane)-co-(dimethylsiloxane) (Mw = 90,000 and 17000) were commercially available from Gelest. Neither was soluble in CO_2 and copolymers with lesser degrees of phenyl methyl siloxane were not available.

7.3 HYDROGEN BONDING COMPOUNDS AND DENDRIMERS

It was postulated that intermolecular associations between small compounds with two hydrogen bonding groups (urea) could yield a viscosity-enhancing linear macromolecular in solution. Therefore a non-fluorous CO_2-philic compound with a core of two ureas separated by a short alkyl chain with two highly acetylated “arms” derived from per-acetylated gluconic acid

was synthesized. This compound, 5R,6R,7S,8R,27R,28S,29R,30R)-5,6,7-triacetoxy-2,9,14,21,26-pentaoxo-3,10,25-trioxa-13,15,20,22-tetraazahentriacontane-8,27,28,29,30,31-hexaylhexaacetate, dissolved to 1wt % in supercritical CO_2 at 298 K and 65 MPa. Although this compound did not induce a viscosity increase, it yielded brittle microfibrillar foam upon depressurization, and also at elevated pressure. The first non-fluorous, first-generation highly CO_2-soluble dendrimer with four per-acetylated "arms" derived from acetylated gluconic acid and a bis-urea core was also synthesized, (5R,6R,7S,8R,27S,28R,29S,30S)-5,6,7,8-tetraacetoxy-2,9,14,21,26-pentaoxo-12-(((2R,3S,4S,5R)-2,3,4,5,6-pentaacetoxy-hexanoyloxy)methyl)-23-(((2S,3R,4S,5S)-2,3,4,5,6-pentaacetoxy-hexanoyloxy)methyl)-3,10,25-trioxa-13,15,20,22-tetraazahentriacontane-27,28,29,30,31-pentaylpentaacetate. This dendrimer was soluble up to 5wt% in liquid and supercritical CO_2 and did not yield brittle foams upon depressurization, probably because the multiple arms resulted in steric hindrance of the hydrogen bonding. These results indicate that acetylation provides an environmentally benign pathway to the generation of small, non-fluorous CO_2-soluble hydrogen-bonding compounds and dendrimers, but such compounds do not thicken CO_2.

8.0 FUTURE WORK

1) Poly (acetoxy acetate) and branched polymers were not soluble in CO_2 at pressure about 69MPa. They polymers melted in dense CO_2 and formed free-flowing liquids, which usually indicates that dissolution will occur at slightly higher pressure. Therefore these polymers must be sent to Clemson University to be tested at higher pressure for there solubility in CO_2.

2) Poly (3-acetoxy oxetane): Molecular modeling suggests that PAO is a potentially CO_2 soluble polymer. The interaction energy values of CO_2 and methoxy isopropyl acetate (representative repeat unit for poly(3-acetoxy oxetane) are greater in magnitude and number that the interaction energy values between CO_2 and isopropyl acetate (representative repeat unit for poly (vinyl acetate)

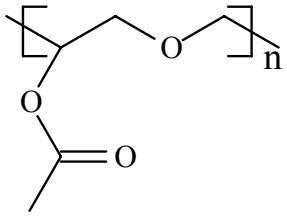


Figure 8.1: Poly (acetoxy oxetane)

Oligomers of poly (3-acetoxy oxetane) were successfully synthesized and were soluble in CO_2. But oligomers/polymer with 10-1000 repeat units are required to provide a more meaningful assessment of this polymer.

2) Aromatic siloxane copolymer: Poly (dimethyl siloxane) (PDMS) is very CO_2 soluble over a wide range of molecular weight. Copolymers (~10% phenyl methyl siloxane)-(dimethylsiloxane) (Mw = 90,000 and 17000) were commercially available from Gelest and was not soluble in CO_2.

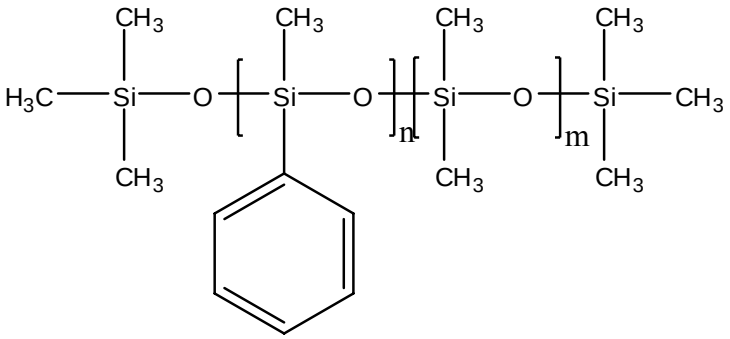


Figure 8.2: Copolymer (8-12% phenyl methyl siloxane)-(dimethylsiloxane)

As we have observed, aromatic vinyl acetate co-polymers with 10% aromatic content are not soluble in CO_2. It would be very interesting to study these polymers with lower aromatic content because in this research we demonstrated that 5mol% phenyl content in a PVAc polymer was sufficient to nearly double the CO_2 viscosity.

4) Surfactants: It may be possible to increase the viscosity of dense, high pressure CO_2 via the self assembly of CO_2-soluble surfactants into rodlike micelles shown in Figure 8.3. These surfactants will have CO_2-philic tails for dissolution and CO_2-phobic head groups. The structure of the surfactant must be carefully designed to promote linear, rather than spherical, micelles. This is most commonly achieved with surfactants that have tails on both sides of the CO_2-phobic group. For example, hydroxyaluminum di(2-ethyl hexanoate) dissolves in liquid propane and thickens liquid propane. It must be noted that subtle changes to the tail structure (e.g. the addition or removal, or change in degree of branching) can result in the surfactant either becoming insoluble, or remaining insoluble but not being capable of thickening the liquid. Dazun Xing is exploring this concept during his PhD studies.

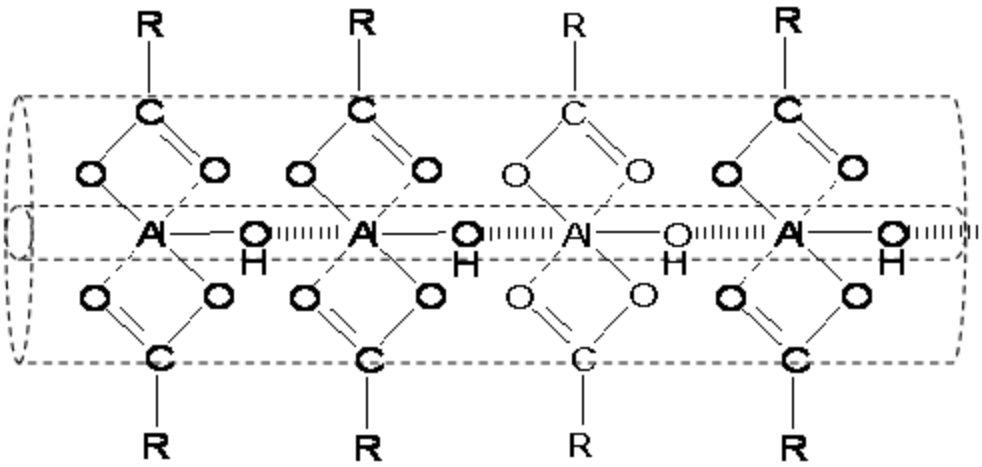


Figure 8.3: Rod-like micelles formation of hydroxyaluminum di (2-ethyl hexanoate)

It may also be possible to design CO_2-soluble surfactants that will decrease the mobility of a CO_2; *not* by increasing the viscosity of CO_2, but rather by making a CO_2 foam or emulsion as the CO_2 + surfactant solution mixes with the brine in the pores of the sandstone or limestone reservoir. The CO_2 would probably be the high volume, discontinuous phase of the emulsion. These foams have a very low mobility (permeability/viscosity) that can enhance the sweep efficiency of the CO_2. ***This appears to be the most promising route for improving the sweep efficiency of CO_2 because it is likely that several non-ionic, commercially available, highly CO_2-soluble surfactants can be used for this purpose at very low concentrations at pressure below the MMP.***

APPENDIX A

PHYSICAL PROPERTIES OF SUPERCRITICAL SOLVENTS

Solvent	Tc(^{o}C)	Pc(bar)	α x 10^{25} (cm^3)	μ (D)
Ethane	32.3	48.8	45	0.0
Propane	96.7	42.5	62.9	0.1
Butane	152.1	38.0	81.4	0.0
Hexane	234.1	29.7	118.3	0.0
Ethylene	9.2	50.4	42.3	0.0
Propylene	91.9	46.2	62.6	0.4
1-Butene	146.5	39.7	82.4	0.3
2-trans-butene	155.5	39.9	84.9	0.0
Dimethyl-ether	126.9	52.4	51.6	1.3
Tetrafluoromethane	-45.6	37.4	28.6	0.0
Hexafluoroethane	19.7	29.8	47.6	0.0
Octafluoropropane	71.9	26.8	66.7	0.0
Hexafluoropropane	94.0	29.0	60.4	0.4
Difluoromethane	78.5	53.4	24.8	2.0

Trifluoromethane	26.2	48.6	26.5	1.6
Chlorotrifluoromethane	28.8	38.7	45.8	0.5
Chlorodifluoromethane	96.2	49.7	44.4	1.4
Difluoroethane	113.1	45.2	41.5	2.3
Tetrafluoroethane	101.1	40.6	43.8	2.1
Carbon-dioxide	31.0	73.8	27.6	0.0

APPENDIX B

[1]NMR OF COMPOUNDS IN CHAPTER 4

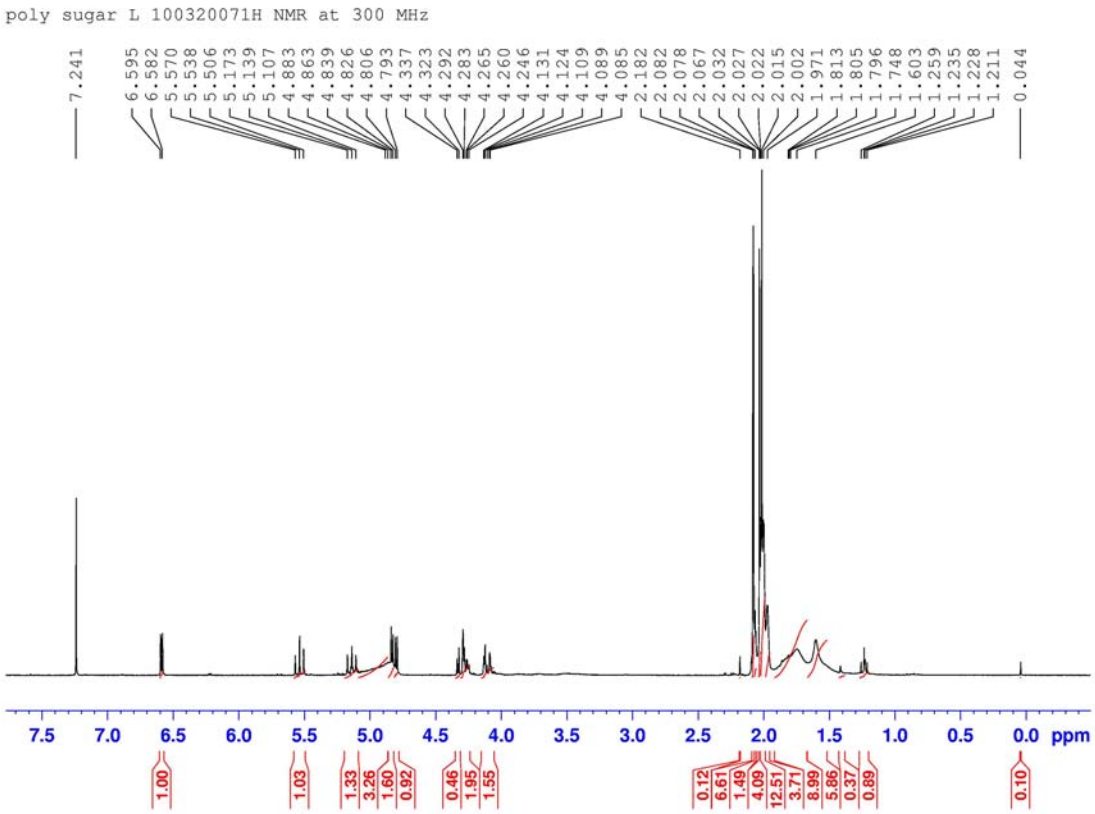


Figure B.1: [1]NMR of P(AcGIcVE) in $CDCl_3$

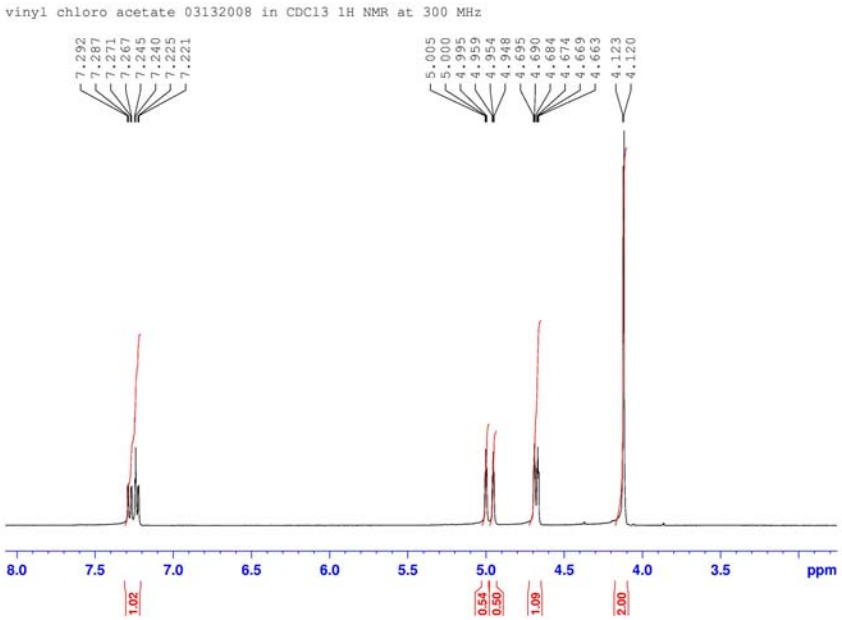


Figure B.2: ^{1}NMR of Vinyl Chloro Acetate in $CDCl_3$

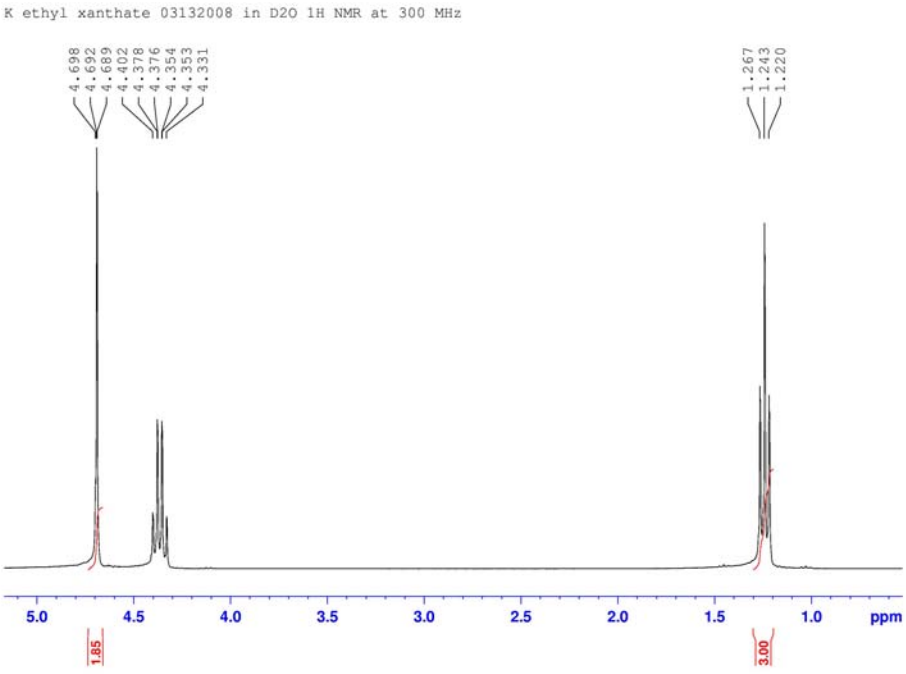


Figure B.3: ^{1}NMR of Potassium ethyl Xanthagonate Acetate in D_2O

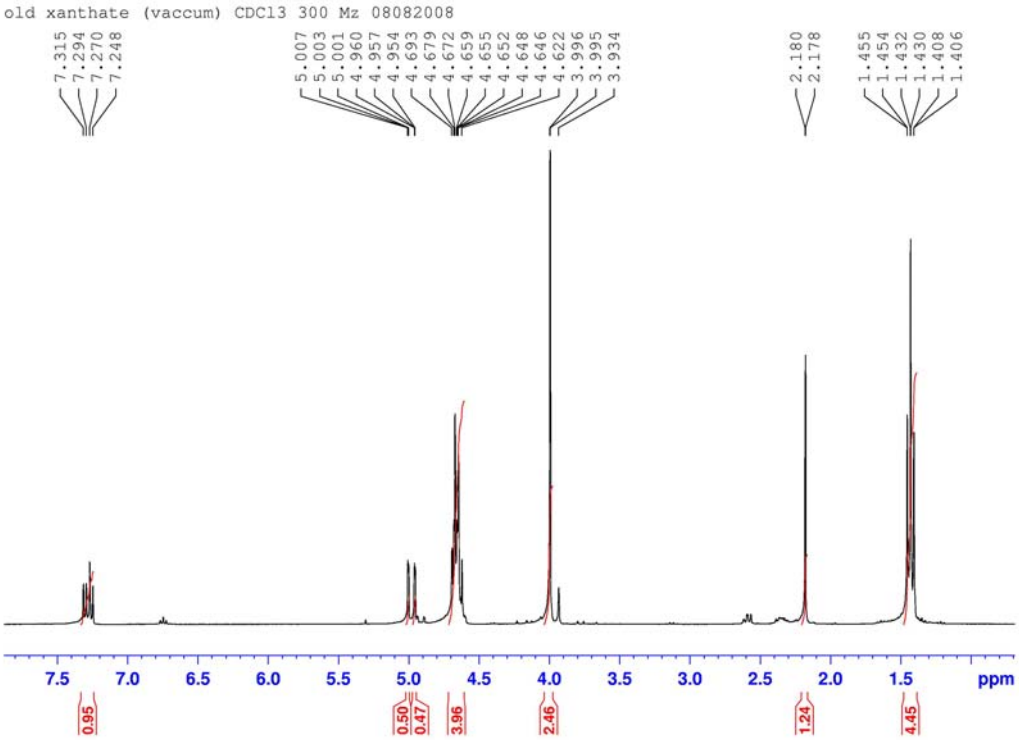


Figure B.4: ^{1}NMR of Cross-linker in $CDCl_3$

APPENDIX C

[1]NMR OF COMPOUNDS IN CHAPTER 6

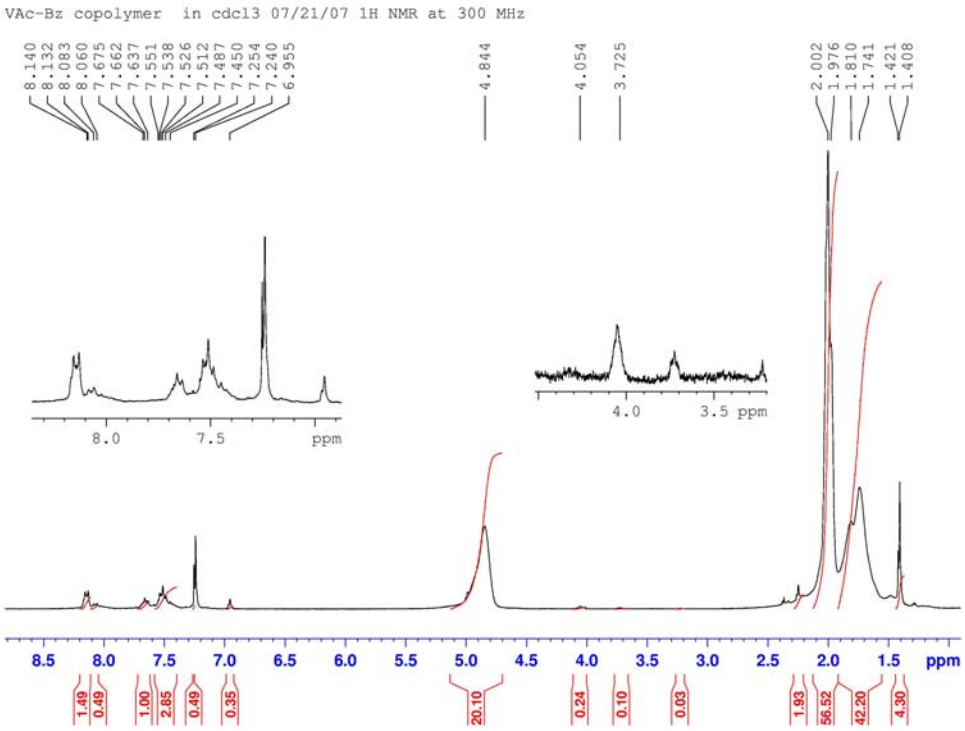


Figure C.1: [1]NMR of Poly (vinyl acetate-co-benzoyl) with 5% aromatic content

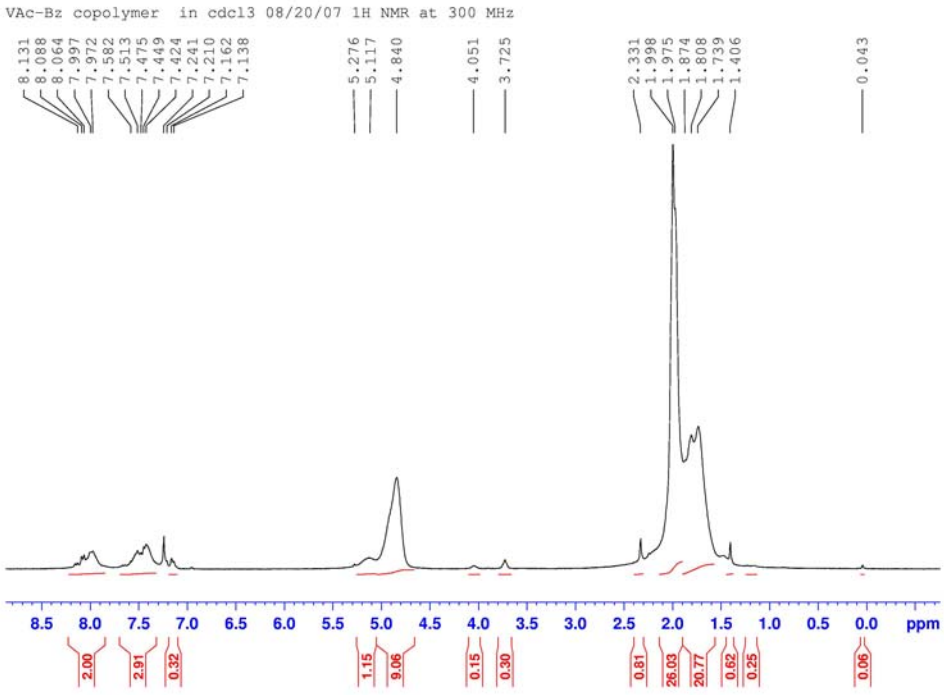


Figure C.2: ^{1}NMR of Poly (vinyl acetate-co-benzoyl) with 10% aromatic content

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